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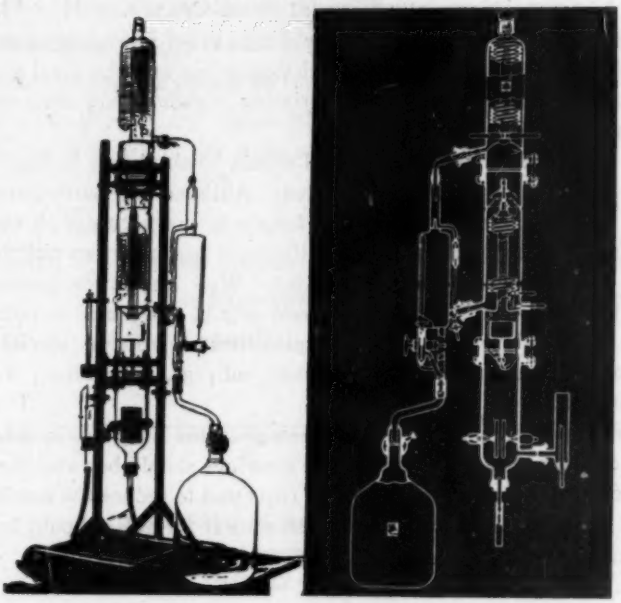

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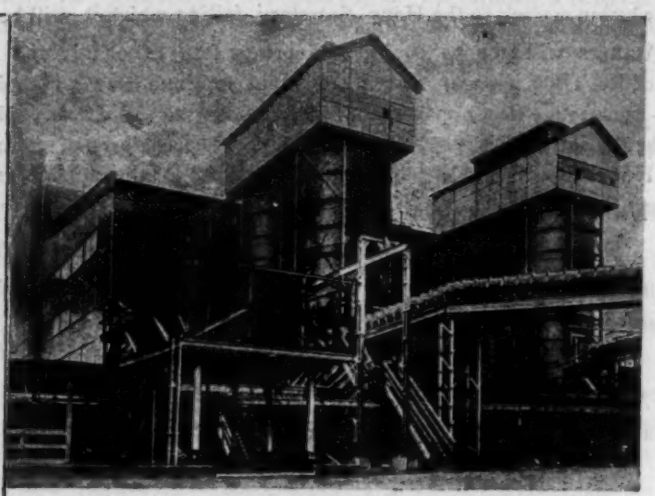

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STUDIES ON THE DEPENDENCE OF OPTICAL ACTIVITY ON CHEMICAL CONSTITUTION. PART XLVIII. THE ROTATORY DISPERSION OF METHYL, ETHYL, PHENYL, *o*-TOLYL, *p*-TOLYL, α-NAPHTHYL AND β-NAPHTHYL *d*-CAMPHOR-β-SULPHONATES

By Bawa Kartar Singh and S. Ramagopala Sarma

The rotatory dispersion of methyl, ethyl, phenyl, *o*- and *p*-tolyl, and α- and β-naphthyl-*d*-camphor-β-sulphonates has been studied in 7 solvents for 13 wave-lengths (λ = 6708 to 4358Å) in the visible region of the spectrum. All the above compounds exhibit simple rotatory dispersion which can be expressed by Drude's one-term equation. The *characteristic*' wave-lengths, λ_os, vary from 3442 to 2600Å in different cases.

In this communication we have discussed the rotatory dispersion of methyl, ethyl, phenyl, *o*-tolyl, *p*-tolyl, α-naphthyl and β-naphthyl *d*-camphor-β-sulphonates in seven solvents.

The rotatory dispersion of these compounds in all the seven solvents can be expressed by Drude's one-term equation, $[\alpha]_\lambda = K/\lambda^2 - \lambda_o^2$, where K is the rotation constant and λ_o^2, the dispersion constant. It is therefore 'simple'.

Out of 627 observations, in as many as 475 the difference between the observed and calculated values of specific rotations corresponds to a deviation of 0.01° or less in the observed angle of rotation and in as many as 140, this deviation lies between 0.01° and 0.03°. In the remaining 12 casses, the difference is 0.04° or above for wave-lengths mostly in the blue region of the spectrum which are difficult to read.

The values of the 'characteristic' wave-lengths, λ_os, vary from 3442 to 2600Å.

It is observed that the alkyl esters generally possess a higher rotatory power than the aryl esters (Tables I to VII), with minor exceptions as in the case of ethyl *d*-camphor-β-sulphonate in benzene and acetone (Table A). Methyl *d*-camphor-β-sulphonate has a higher rotatory power than the corresponding ethyl derivative with minor variations (Tables I and II). *o*-Tolyl and α-naphthyl *d*-camphor-β-sulphonates show higher specific rotations than their *para* and β-isomers respectively in all solvents (Tables IV to VII).

Position Isomerism and Rotatory Power

The specific rotatory powers, $[\alpha]^{33}_{5461}$, of the seven esters described above in seven solvents are recorded in Table A.

The effect of position isomerism on optical rotatory power could not be completely studied, as *m*-tolyl *d*-camphor-β-sulphonate was gummy in consistency and could not be isolated in a pure condition. It is, however, found that the *para* isomer has a lower rotatory power than the *ortho* isomer in all solvents. The sequence of the decreasing order of the rotatory powers is $o > un > p$ in chloroform, ethyl acetate, acetone and methyl alcohol, whereas it is $un > o > p$ in benzene, pyridine and ethyl alcohol.

It does not therefore support Frankland's *lever-arm* hypothesis (*J. Chem. Soc.* 1896, **69**, 284).

TABLE A

Specific rotatory powers of the ester for Hg_{5461} *at* 35° *in different solvents.*

Esters of *d*-camphor-β-sulphonic acid.	Benzene. *(2.28)	Chloroform (5.2)	Ethyl acetate (6.11)	Pyridine. (12.4)	Acetone. (21.5)	EtOH. (25.8)	MeOH (31.5)
Methyl	64.00	55.00	60.00	52.50	55.00	49.00	48.00
Ethyl	59.50	56.00	60.50	53.00	49.00	45.00	45.00
Phenyl	64.50	47.00	53.50	50.50	49.50	43.00	40.50
o-Tolyl	59.00	48.00	54.50	47.50	50.00	41.00	41.00
p-Tolyl	57.50	43.50	45.50	41.50	39.00	40.00	32.50
α-Naphthyl	58.50	52.50	57.50	52.50	54.50	41.00	41.00
β-Naphthyl	55.50	45.50	48.50	43.50	41.00	40.00	36.00

* Figures in simple brackets indicate the dielectric constants of the solvents.

Influence of Solvent on Rotatory Power

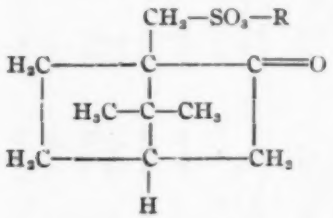
It is found that the magnitude of the dielectric constants of the solvents and that of the rotatory power of these esters in solution in them run generally in the opposite direction with minor variations (Table A): the order of the decreasing rotatory power in different solvents is benzene (2.28,* > ethyl acetate (6.11) > chloroform (5.2) > pyridine (12.4) > ethyl alcohol (25.8) > methyl alcohol (31.5), except in the case of phenyl ester where the positions of pyridine and chloroform are interchanged. Acetone (21.5), however, behaves abnormally in almost half the cases investigated.

The 'Characteristic' Wave-lengths, λ_0*s, of the Esters of* d*-Camphor-β-sulphonic Acid in Different Solvents*

As already mentioned above, the values of the 'characteristic' wave-lengths, λ_0s, of the esters in different solvents vary from 3442 to 2600Å. These values, deduced from Tables I to VII, are shown in Table B.

* The figures in brackets are the dielectric constants of the solvents.

On examination of the structural formula of the esters,



it is found that there is only one chromophore, the keto group, $>C=O$, which has a 'characteristic' wave-length of about 2800Å in the ultraviolet region of the spectrum.

A study of Table B reveals that the 'characteristic' wave-lengths corresponding to this value (2800Å) are found only in a few cases, as indicated below (and shown underlined in Table B): Ethyl ester in chloroform (2922 Å) and ethyl acetate (2917 Å), phenyl ester in benzene (2600 Å), α-naphthyl ester in benzene (2985 Å), ethyl acetate (2990 Å) and pyridine (2989 Å) and β-naphthyl ester in benzene (2896 Å).

Thus out of 49 cases recorded above, only in 7 cases the 'characteristic' wave-lengths correspond to the ultraviolet absorption band of the ketonic group. In the remaining cases, λ_0 lies between 3442 and 3014 Å.

TABLE B

The values of the characteristic wave-lengths of the esters in different solvents.

Esters of *d*-camphor-β-sulphonic acid.	Benzene.	$CHCl_3$.	Ethyl-acetate.	Pyridine.	Acetone.	EtOH.	MeOH.
Methyl	3123	3135	3116	3293	3195	3142	3198
Ethyl	3065	2922	2917	3412	3195	3318	3051
Phenyl	2600	3068	3135	3232	3066	3196	3258
o-Tolyl	3135	3231	3217	3266	3241	3178	3162
p-Tolyl	3014	3231	3152	3239	3345	3251	3124
α-Naphthyl	2985	3047	2990	2989	3302	3402	3163
β Naphthyl	2896	3165	3057	3152	3113	3148	3113

TABLE I

Rotatory dispersion of methyl d-*camphor-β-sulphonate* (m.p. 61°) *at* 35°.

Solvents:		Benzene		Chloroform		Ethyl acetate		Pyridine		Acetone		Ethyl alcohol		Methyl alcohol	
		* (2.28)		(5.2)		(6.11)		(12.4)		(21 5)		(25.8)		(31.5)	
Conc (g./100 c.c.)		1.00		1 00		1.00		1.00		1.00		1.00		1.00	
Calc.	$[\alpha]^{35}_{\lambda}$	$\frac{13.20}{\lambda^2-0.0932}$		$\frac{10.90}{\lambda^2-0.1021}$		$\frac{12.06}{\lambda^2-0.0972}$		$\frac{10\ 03}{\lambda^2-0.1084}$		$\frac{10.90}{\lambda^2-0.1021}$		$\frac{9.860}{\lambda^2-0.0987}$		$\frac{9.386}{\lambda^2-0.1023}$	
	λ_0 ... (Å)	3123		3195		3116		3293		3195		3142		3198	
Lines.		*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*
6708		37.co	36.77	31.50	31.33	34 50	34.22	29.50	29.35	31.00	31 33	28.50	28.06	27.50	27.00
6438		40.50	40.83	35.00	34 88	37.50	38.co	33.00	33.24	34.50	34.88	31.00	31.23	31.00	31.48
6104		47.00	47 00	40.00	40.31	44 00	43.80	38.00	37.96	40.50	40.31	36.00	36.00	34.00	34.73
5893		52.00	51.65	45.00	44.44	48.50	48.23	42.00	42.00	45 00	44 44	40 50	39.68	38.00	38 32
5780		55.00	54.46	47.00	46.98	51.00	50.83	45.00	44.42	47 00	46.98	42.00	41.89	40.50	40 50
5468		64.00	63.72	55.co	55.35	59.50	59 75	52.00	52.61	55.00	55 35	49.50	49.23	48.00	47.71
5461		64.00	64.00	55.co	55.58	60.00	60.00	52.50	52.82	55.00	55 58	49.00	40.42	48.00	47.92
5209		73.co	73.67	64.00	64.42	69.00	69.28	62.00	61.56	64 50	64.42	56.50	57.12	55 00	55.52
5086		80.00	79.67	70.00	69.60	74.00	74.52	67.00	66.73	70.00	69.60	61.50	61.63	60.00	60 02
4800		94.50	95.26	81.00	84 61	89.50	90.18	81.00	81.68	84.50	84.61	75.00	74.42	72.50	72 98
4678		104.50	104.30	93.50	93.30	99 50	99.10	90.co	90.76	93.50	93.30	81.50	82.04	80 50	80.50
4603		110.00	110.60	98.50	99.33	105.00	105.20	97.00	97.00	99.00	99 33	88.50	87.18	86 00	85 70
4358		136.50	135 50	124.00	124.03	131.50	130 90	...	...	124 00	124.00	108.00	108.00	107.00	107.00

* Figures in brackets in this and the following tables give the dielectric constants of the solvents.

TABLE II

Rotatory dispersion of ethyl d-camphor-β-sulphonate (m.p. 47°) *at* 35°.

Solvents:		Benzene (2.28)		Chloroform (5.2)		Ethyl acetate (6.11)		Pyridine (12.4)		Acetone (21.5)		Ethyl alcohol (25.8)		Methyl alcohol (31.5)	
Conc. (g./100 c.c.)		1.00		1.00		1.00		1.00		1.00		1.00		1.00	
Calc.	$[\alpha]^{35}_{\lambda}$	$\frac{12.25}{\lambda^2-0.0939}$		$\frac{11.92}{\lambda^2-0.0854}$		$\frac{12.85}{\lambda^2-0.0851}$		$\frac{9.529}{\lambda^2-0.1184}$		$\frac{9.599}{\lambda^2-0.1021}$		$\frac{8.504}{\lambda^2-0.1101}$		$\frac{9.407}{\lambda^2-0.0931}$	
	λ_0(Å)	3065		2922		2917		3442		3195		3318		3051	
Lines.		*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o*	*c.*	*o.*	*c.*	*o.*	*c.*
6708		35.00	34.40	32.50	32.69	35.50	34.92	28.50	27.92	28.00	27.59	25.00	25.02	26.00	26.35
6438		38.50	38.21	36.00	36.21	39.00	39.30	32.00	32.18	30.50	30.73	27.00	27.94	29.00	29.26
6104		43.50	43.97	42.00	41.52	44.50	44.70	37.50	37.50	35.50	35.50	32.50	32.40	33.00	33.64
5893		48.50	48.36	45.50	45.50	49.50	49.01	41 50	41.65	40.00	39.16	36.00	35.86	37.00	37.00
5780		51.00	51.00	48.00	47.93	51.00	51.59	45.00	44.18	41.50	41.38	38.00	38.co	39.00	39.00
5468		59.50	59.73	56.00	55.81	59.50	60.01	52.50	52.76	48.50	48.75	44.50	45.02	45.50	45.67
5461		59.50	59.96	56.00	56.02	6c.50	60.28	53.00	53.00	49.co	48.95	45.00	45.21	45.50	45.84
5209		69.50	69.05	64.50	64.12	68.50	68.99	62.50	62.32	56.00	56.73	53.00	52.75	53.00	52.76
5086		74.00	74.33	68.00	68.78	73.50	74.00	68.50	67.92	61.50	61.30	58.00	57.23	56.50	56.81
4800		90.00	89.74	82.00	82.21	89.00	88.41	85 00	85.00	74.50	74.82	71.00	70.63	68.50	68.41
4678		98.50	98.00	89.50	89.29	96.00	96.00	94.5	94.91	83.00	82.18	77.50	78.16	75.00	74.72
4603		103.50	103.90	94.50	94.30	101.50	101.40	...	...	87.50	87.50	83.00	83.62	79.50	79.84
4358		127.50	127.50	114.00	114.00	123.00	122.50	...	...	109.00	109.20	106.50	106.53	97.00	97.00

TABLE III

Rotatory dispersion of phenyl d-*camphor-β-sulphonate* (m.p. 38°) *at* 35°.

	Benzene (2.28)		Chloroform (5.2)		Ethyl acetate (6.11)		Pyridine (12.4)		Acetone (21.5)		Ethyl alcohol (25.8)		Methyl alcohol (31.5)	
Conc. (g./100 c.c.)	1.00		1.00		1.00		1.00		1.00		1.00		1.00	
Calc. $[\alpha]_{\lambda}^{35}$ ...	$\frac{15.06}{\lambda^2-0.0675}$		$\frac{9.591}{\lambda^2-0.0941}$		$\frac{10.87}{\lambda^2-0.0984}$		$\frac{9.782}{\lambda^2-0.1045}$		$\frac{10.08}{\lambda^2-0.0940}$		$\frac{8.351}{\lambda^2-0.1021}$		$\frac{7.716}{\lambda^2-0.1061}$	
λ_0 (Å) ...	2600		3068		3135		3232		3066		3196		3258	
Lines.	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*
6708	39.50	39.38	26.50	26.95	30.50	30.60	29.00	28.31	28.50	28.31	24.00	24.01	22.00	22.43
6438	44.00	43.41	29.50	29.93	34.00	34.00	31.00	31.55	32.00	31.46	26.50	26.73	25.00	25.02
6104	49.00	49.39	35.00	34.45	39.50	39.14	36.50	36.50	36.00	36.19	31.00	30.88	29.00	29.01
5893	53.50	53.86	38.00	37.89	42.50	43.07	40.00	39.57	39.50	39.81	33.50	34.07	32.00	32.00
5780	56.50	56.50	40.00	39.97	45.50	45.50	42.50	42.60	42.00	42.00	36.00	36.00	34.00	33.84
5468	64.50	65.08	47.00	46.81	53.50	53.23	50.00	50.29	49.50	49.17	42.50	42.41	39.50	40.00
5461	64.50	65.31	47.00	47.00	53.50	53.44	50.50	50.50	49.50	49.36	43.00	42.59	40.50	40.17
5209	74.00	73.93	54.00	54.12	61.00	61.59	59.00	58.65	57.00	56.85	49.00	49.36	47.00	46.17
5086	79.00	78.81	58.00	58.27	67.00	66.32	64.00	63.44	61.50	61.28	52.50	52.32	50.00	50.56
4800	93.00	92.51	70.50	70.37	80.50	80.16	77.50	77.70	73.50	73.90	65.50	65.09	62.00	62.08
4678	98.00	98.37	76.50	76.85	85.50	85.90	86.00	85.51	80.00	80.70	72.00	71.50	69.00	68.40
4603	104.00	104.40	81.00	81.49	92.50	92.50	...	...	86.00	85.57	76.00	76.13	73.00	73.00
4358	123.00	123.00	100.00	100.00	114.00	114.00	...	...	105.00	105.00	95.00	95.00	91.50	91.97

TABLE IV

Rotatory dispersion of o-*tolyl* d-*camphor-β-sulphonate* (m.p. 58°) *at* 35°.

		Benzene (2.28)		Chloroform (5.2)		Ethyl acetate (6.11)		Pyridine (12.4)		Acetone (21.5)		Ethyl alcohol (25 8)		Methyl alcohol (31.5)	
Conc. (g./100 c.c.)		1.00		1.00		1.00		1.00		1.00		1.00		1.00	
Calc.	$[\alpha]_\lambda^{35}$	$\frac{11.57}{\lambda^2-0.0984}$		$\frac{9.352}{\lambda^2-0.1043}$		$\frac{10.57}{\lambda^2-0.1035}$		$\frac{9.008}{\lambda^2-0.1067}$		$\frac{9.438}{\lambda^2-0.1050}$		$\frac{8.150}{\lambda^2-0.1009}$		$\frac{8.050}{\lambda^2-0.1000}$	
	λ_0 (Å)	3135		3231		3217		3266		3241		3178		3.62	
Lines.		o	c	o	c	o	c	o	c	o	c	o	c	o	c
6708		33.00	32.9	27.00	27.1	31.00	30.5	26.50	26 51	27.00	27.36	23.00	23.38	23.00	23.00
6438		37.00	36.6	30.00	30 2	34.00	34.0	30.00	29.57	30.50	30.50	25.50	25.99	25. 0	25.61
6104		42.50	43.2	34.50	34.9	40.00	39.3	34.00	34.28	35.00	35.29	30 00	30.00	30.00	29 54
5893		46.50	46.5	38.50	38.5	44.00	43 4	38 10	37.84	39 50	38.97	33.50	33.09	32 00	32 56
5790		50.00	49.1	41.00	40.7	47.00	45.9	40 00	40.01	41.50	41.20	35.50	34.94	35.00	34.39
5468		59.00	57.7	48.00	48.0	54.50	54.1	47.50	47.32	48.50	48.65	41.50	41 30	40.50	40.44
5461		59.00	57.0	48.00	48.2	54.50	54.3	47.50	47.52	50.00	48.85	41.00	41.44	41.00	40.62
5209		67.00	66.9	56.00	56.0	63.00	63.0	55.50	55.21	56.00	56.75	47.50	47.83	47 00	46 89
5086		73.50	72.2	60.00	60.6	67.50	68 1	60.50	59.87	60 00	61.45	52.50	51.65	49.50	50.71
4800		87.00	87.3	74.50	73.9	82.00	83.0	74.50	73.77	74.50	74.98	62.00	62 70	62.00	61.52
4678		96.00	96.0	82.00	81.6	92.00	91.7	81.50	81.10	85.00	82.87	69.00	69.07	67.00	67.69
4603		101.50	102.1	89.50	87.5	96.00	97.6	86.50	86.18	87.50	88.37	73.50	73.50	72.00	72.00
4358		124.00	126.3	110.50	109.1	120.5	122.2	...	...	111.00	110.00	91.00	91.58	89.00	89.45

TABLE V

Rotatory dispersion of p-*tolyl* d-*camhor-β-sulphonate* (m.p. 64°) *at* 35°.

		Benzene (2.28)		Chloroform (5.2)		Ethyl acetate (6.11)		Pyridine (12.4)		Acetone (21.5)		Ethyl alcohol (25.8)		Methyl alcohol (31.5)	
Conc. (g./100 c.c.)		1.00		1.00		1.00		1.00		1.00		1.00		1.00	
Calc.	$[\alpha]\lambda^{35}$ ...	$\frac{11.98}{\lambda^2-0.0983}$		$\frac{8.377}{\lambda^2-0.1044}$		$\frac{9.068}{\lambda^2-0.0993}$		$\frac{8.022}{\lambda^2-0.1049}$		$\frac{7.264}{\lambda^2-0.1119}$		$\frac{7.661}{\lambda^2-0.1054}$		$\frac{6.623}{\lambda^2-0.0976}$	
	λ_0(Å) ...	3014		3231		3152		3239		3345		3251		3124	
Lines.		*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*
6708		33.50	33.35	24.00	24.24	26.00	25.86	24.00	23.25	22.00	21.50	22.50	22.23	18.50	18.79
6438		37.50	37.01	27.00	27.01	28.50	28.77	25.50	25.91	24.00	24.00	24.00	24.78	21.50	21.90
6101		42.50	42.50	31.00	31.23	33.00	33.18	30.50	29.97	28.00	27.86	29.50	28.67	24.00	24.08
5893		47.00	46.72	34.50	34.50	37.00	36.58	32.50	33.11	31.00	30.81	32.00	31.68	26.00	26.53
5780		49.00	49.24	36.00	36.47	38.50	38.50	35.00	35.00	32.50	32.59	33.50	33.50	28.00	28.00
5468		57.00	57.54	43.00	43.22	45.00	45.41	41.00	41.33	38.50	38.82	40.00	39.57	32.50	32.08
5461		57.50	57.76	43.50	43.40	45.50	45.59	41.50	41.50	39.00	39.00	40.00	39.76	32.50	33.02
5209		66.00	66.37	50.50	50.19	53.00	52.72	48.00	48.21	46.00	45.57	46.00	46.17	38.50	38.13
5086		71.00	71.35	55.00	54.29	56.50	56.89	52.50	52.16	50.00	49.55	50.00	49.97	41.50	41.14
4800		86.00	85.51	66.00	66.22	69.00	69.43	64.00	63.87	60.50	61.04	60.50	61.05	49.50	49.68
4678		94.00	93.52	73.50	73.23	76.00	75.82	71.00	70.37	67.50	67.95	67.50	67.05	54.00	54.60
4603		99.00	99.00	78.00	78.00	81.00	80.60	...	...	72.00	72.71	72.00	72.00	58.00	58.00
4358		120.50	120.80	98.00	97.86	100.00	100.00	...	...	93.00	93.00	91.00	91.00	72.00	71.68

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TABLE VI

Rotatory dispersion of α-naphthyl d-camphor-β-sulphonate (m.p. 115°) *at* 35°.

	Benzene (2.28)		Chloroform (5.2)		Ethyl acetate (6.11)		Pyridine (12.4)		Acetone (21.5)		Ethyl alcohol (25.8)		Methyl alcohol (31.5)	
Conc. (g./100 c.c.)	1.00		1.00		1.00		1.00		1.00		0.50		1.00	
Calc. $[\alpha]\lambda^{35}$ ...	$\frac{12.27}{\lambda^2-0.0891}$		$\frac{10.77}{\lambda^2-0\ 0928}$		$\frac{11.97}{\lambda^2-0.0898}$		$\frac{10.95}{\lambda^2-0.0894}$		$\frac{10.28}{\lambda^2-0\ 1090}$		$\frac{7.473}{\lambda^2-0.1158}$		$\frac{8.154}{\lambda^2-0.1004}$	
Calc. λ_o(Å) ...	2985		3047		2990		2989		3302		3402		3163	
Lines.	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*
6708	34.00	34.00	30.00	30.16	34.00	33.24	31.00	30.45	30.00	30.14	22.00	21.69	23.50	23.31
6438	38.00	37.70	33.50	33.38	36.50	36.89	34.00	33.69	33.50	33.64	25.00	25.02	26.00	25.93
6104	43.00	43.33	38.50	38.50	42.00	42.35	38.00	38.68	39.00	39.00	29.00	29.14	30.00	29.93
5893	48.00	47.53	42.50	42.35	46,50	46.50	42.50	42.48	43.50	43.14	32.50	32.29	33.00	33.00
5780	50.50	50.07	45.00	44.65	49.00	49.00	44.50	44.76	46.00	45.65	34.00	34.23	34.00	34.85
5468	58.50	58.45	52.50	52.24	57.50	57.23	52.50	52.25	54.00	54.09	41.00	40.79	41.00	41.02
5461	58.50	58.68	52.50	52.44	57.50	57.40	52.50	52.47	54.50	54.31	41.00	40.98	41.00	41.18
5209	67.50	67.33	60.00	60.36	65.50	65.95	60.50	60.22	63.00	63.33	47.50	48.06	47.50	47.62
5086	72.50	72.33	65.50	64.92	70.50	70.86	64.50	64.69	68.50	68.64	52.00	52.30	51.00	51.40
4800	85.50	86.54	79.00	78.00	85.00	84.84	77.50	77.41	84.50	84.33	65.00	65.07	62.50	62.36
4678	94.50	94.50	86.00	85.43	92.50	92.72	85.00	84.57	9.250	93.50	72.00	72.49	68.00	68.63
4603	100.00	100.00	90.50	90.50	98.00	98.11	87.00	85.52	100.00	100.00	78.00	77.84	73.00	73.03
4358	121.00	121.60	113.00	110.90	120.50	119.50	...	...	125.00	126.90	100.0	100.7	90.50	90.69

TABLE VII

Rotatory dispersion of β-naphthyl d-*camphor-β-sulphonate* (m.p. 100°) *at* 35°.

		Benzene		Chloroform		Ethyl acetate		Pyridine		Acetone		Ethyl alcohol		Methyl alcohol	
		(2.28)		(5.2)		(6.11)		(12.4)		(21.5)		(25.8)		(31.5)	
Conc. (g./100 c.c.)		1.00		1.00		1.00		1.00		1.00		1.00		1.00	
Calc.	$[\alpha]\lambda^{35}$ ...	$\frac{11.83}{\lambda^2-0.0839}$		$\frac{9.017}{\lambda^2-0.1002}$		$\frac{9.786}{\lambda^2-0.0935}$		$\frac{8.668}{\lambda^2-0.0993}$		$\frac{8.265}{\lambda^2-0.0969}$		$\frac{7.870}{\lambda^2-0.0991}$		$\frac{7.168}{\lambda^2-0.0969}$	
	λ_0(Å) ...	2896		3165		3057		3152		3113		3148		3113	
Lines.		*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*	*o.*	*c.*
6708		32.50	32.3	26.00	25.8	27.50	27.5	25.00	24.7	23.00	23.4	22.00	22.4	20.00	20 3
6438		36.50	35.8	28.50	28.7	30.50	30.5	27.50	27.5	25.50	26.0	24 50	25.0	23.00	22.6
6104		41.00	41.0	33.00	32.7	35.50	35.1	32.00	31.8	30.00	30.0	29.00	28.8	26.00	26.0
5893		44.50	44.9	36.50	36.5	39.00	38.6	35.00	35.0	33.00	33.0	32.00	31.7	28.50	28.6
5780		48.00	48.4	38.50	38.5	41.00	40.7	37.00	36.0	35.00	35.2	33.50	33.5	30.00	30.2
5468		55.00	55.0	45 00	45.5	48.00	47.6	43.00	43.4	41 50	40.9	39.50	39.5	36.00	35.6
5461		55.50	55.2	45.50	45.8	48.50	47.7	43.50	43.6	41.00	41.0	40.00	39.6	36.00	36.0
5209		63.00	63.1	52.00	52.7	55.00	55.0	49.50	50.4	47.00	47 4	46.00	45.7	40.00	41.0
5086		69.00	67.7	56.00	56.9	60.00	59.2	54.00	53.4	51.00	51.1	49.00	49.3	44.00	44.3
4800		82.00	80.5	69.00	69 0	73.00	71.2	66.50	65.8	62.50	61.7	59.50	59.7	54.00	53.5
4678		87.50	87.1	76.00	76.0	78.00	78.0	72.50	72.5	67.50	67.8	66.00	65.7	59.00	59.0
4603		92.50	92.5	81.50	80.8	83.00	82.7	78.50	79.1	72.00	72.0	70.03	69.9	64.50	62.4
4358		112.50	111.6	100.00	100.4	103.00	101.1	...	...	90 00	89 0	86.50	86.6	77.00	79.3

Our results on the determination of the ultraviolet absorption maxima, λ_{max}, of these esters (unpublished work) provide values of λ_{max} ranging from 2890 to 2600 Å. It is therefore not clear to what absorption bands the 'characteristic' wave-lengths (λ_os) ranging between 3442 and 3014 Å (Table B) correspond. They do not agree with the value of $\lambda_{max.}$ as found by us. The elucidation of this discrepancy is still awaited. Its solution will throw light on the validity of Drude's equation, $[\alpha]_\lambda = \Sigma K/\lambda^2 - \lambda_o^2$, in which λ_os are the ultraviolet absorption bands controlling rotation.

EXPERIMENTAL

The esters will be described by us in a separate communication.

The rotatory dispersion measurements were carried out in a 2-dcm jecketed tube at 35° in seven solvents for 13 wave-lengths in the visible part of the spectrum (λ=6708 to 4358 Å). The values of λ_os, calculated from the dispersion formulae, are shown in Tables I to VII.

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ORGANIC CHEMISTRY RESEARCH SECTION,
BANARAS HINDU UNIVERSITY,
VARANASI.

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SOME SIX-CO-ORDINATED COMPLEXES OF NICKEL(II): NITRITO-AMMINES OF NICKEL(II)

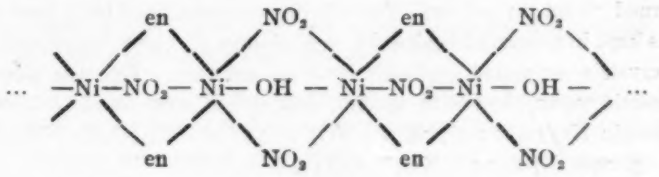
By Debabrata Bandyopadhayay(Banerjea)

Several nitrito-ammines of nickel(II) have been prepared, viz., Ni $[o\text{-}C_6H_4(NH_2)_2]_2$ $(NO_2)_2$, $Ni[C_6H_5\text{-}CH_2NH_2]_4(NO_2)_2$ and $Ni_2[H_2NCH_2CH_2NH_2]_2(NO_2)_3(OH)$. These are all red in colour, insoluble in water and paramagnetic with a moment of about 3 Bohr magnetons. These are believed to be six-co-ordinated nickel(II) complexes, and a polynuclear structure has therefore been assigned to the ethylenediamine complex.

Nitrito-ammines of nickel(II) of the type $Ni(NO_2)_2B_4$, where $B=NH_3$ or C_5H_5N, are already known (Erdmann, *J. prakt. Chem.*, 1866, *i*, **97**, 385; Abegg, 'Handbuch der anorganischen Chemie", Vol. 4, Part iv, No. 1, pp. 690, 731, Verlag von S. Hirzel in Leipzig, 1937). Although the crystals of the pyridine compound are bluish green in colour, the ammonia compound forms beautiful cherry-red crystals. The colour is peculiar to this salt and this was remarked upon by Ephraim (*Ber.*, 1913, **46**, 3101) who assigned to it the constitution $Ni^{II}(NH_3)_4(NO_2)_2$. The magnetic moment of this complex compound was measured by Nyholm (cf. Palmer, "Experimental Inorganic Chemistry", p. 561, Cambridge University Press, Cambridge, 1954) who found this to be paramagnetic with $\mu=3.09$ Bohr magnetons. Since, it is rather well known (Pauling, "The Nature of the Chemical Bond", pp. 119, 122, 123, Cornell University Press, Ithaca, 1948; Rây, "The Theory of Valency and the Structure of Chemical Compounds", p. 52, Indian Association for the Cultivation of Science, Calcutta, 1946) that in the four-covalent complexes of nickel(II) those with red, reddish brown or yellow colour are diamagnetic, while those with blue, bluish green or green colour are paramagnetic, it may safely be assumed that $Ni(NH_3)_4(NO_2)_2$ contains six-covalent nickel(II), as was suggested earlier by Ephraim (*loc. cit.*). This possibly contains d^2sp^3 or sp^3d^2 bonds, presumably the latter type where the two unpaired electrons have not been raised to an outer level. In either case, there should be two unpaired electrons to account for the observed moment of 3.09 Bohr magnetons.

This paper contains a report on the preparations and properties of several other six-co-ordinated nickel(II) complexes which have been carried out in this laboratory. Of the various amines that have been studied, only *o*-phenylenediamine, benzylamine and ethylenediamine have been found to give rise to red coloured insoluble complexes by interaction with nickel salts in presence of an excess of sodium nitrite in aqueous solution. However, methylamine, ethylamine, diethylamine, ethanolamine and *cyclo*-hexylamine failed to produce any such nickel complex, but instead formed a precipitate of green nickel hydroxide on adding to a solution of a nickel salt (sulphate, chloride or acetate) containing a large excess of sodium nitrite. The *o*-phenylenediamine and benzylamine complexes have the composition $Ni[o\text{-}C_6H_4(NH_2)_2]_2(NO_2)_2$ and $Ni(C_6H_5\text{-}CH_2NH_2)_4(NO_2)_2$ respectively. The ethylenediamine compound, however, is somewhat

different and unlike the previous two compounds it separates gradually from a solution of the constituents on long standing. Analysis of nickel, total nitrogen and nitrite indicates a composition $Ni_2[C_2H_4(NH_2)_2]_2(NO_2)_3(OH)$. All the three compounds are red in colour, insoluble in water, and are paramagnetic with a moment of about 3 Bohr magnetons. These therefore possibly contain six-co-ordinated nickel(II). The following polynuclear structure might be suggested for the ethylenediamine complex :



(en = $H_2N.CH_2.CH_2.NH_2$).

The other two compounds have a simple structure analogous to that of the ammonia compound, already referred to.

EXPERIMENTAL

Dinitro-bis-*o*-*phenylenediamine-nickel*(II).—A solution of nickel acetate (6 g.) in water (30 c.c.) was mixed with *o*-phenylenediamine (5.5 g.) in alcohol (40 c.c.). This was cooled in an ice-bath and to it was gradually added with stirring a solution of 25 g. of sodium nitrite in 30 c.c. of water. Stirring was continued for 15 minutes in the cold and thereafter the red coloured precipitate of the nickel complex was filtered off in a Büchner funnel under suction, washed thoroughly with ice-cold water and finally with alcohol, and then dried in vacuo over fused calcium chloride. {Found : Ni, 16.00 ; N, 23.63. $Ni[o\text{-}C_6H_4(NH_2)_2]_3(NO_2)_2$ requires Ni, 16.01 ; N, 22.91%}.

The substance is a red powder, insoluble in ethyl alcohol, ether, acetone and chloroform. It is insoluble in cold water but is decomposed by hot water as well as by alkalies, forming green nickel hydroxide. It is also decomposed by acids, aqueous ammonia and ethylenediamine, forming clear solutions. The compound is paramagnetic: $\chi_g = 10\ 28 \times 10^{-6}$; $\chi_m(cor.) = 3873 \times 10^{-6}$; $\mu_B = 3.09$.

Dinitrito-tetrakis-*benzylamine-nickel*(II).—A solution of nickel acetate (5 g.) and sodium nitrite (20 g.) in water (150 c.c.) was warmed on the water-bath and to it was added slowly with stirring benzylamine (9 c.c.). After the addition of the last drop the mixture, containing the red precipitate of the nickel complex, was kept on the water-bath for 15 minutes more and then filtered under suction as usual. The red solid was washed with an ice-cold solution of very dilute ammonia (approx. 0.3*N*) and then dried in vacuo over fused calcium chloride. (Found : Ni, 10.36 ; N, 14.89. $Ni(C_6H_5CH_2NH_2)_4(NO_2)_2$ requires Ni, 10.14 ; N, 14.52%).

The substance is a red powder, insoluble in ethyl alcohol or ether in the cold but is decomposed on warming with the solvent. It is also decomposed slowly by acetone, chloroform, etc., forming a greenish turbidity, and more readily by water even in the cold,

forming nickel hydroxide, although stable to even hot water containing benzylamine and excess of sodium nitrite. It is decomposed as usual by acids, alkalies, aqueous ammonia, ethylenediamine, etc. It is paramagnetic : $\chi_g = 5.48 \times 10^{-6}$; χ_m (cor.) $= 3361 \times 10^{-6}$; $\mu_B = 2.88$.

$Ni_2(en)_2(NO_2)_3(OH)$.—A solution of nickel acetate (5 g) and sodium nitrite (20 g.) in water (50 c.c.) was cooled in an ice-bath and a concentrated aqueous solution of ethylenediamine was added dropwise with stirring till the dark green solution turned violet in colour. The stirring was continued for 1 hour and the clear solution was kept in a covered beaker for several days at room temperature (about 25°) when red crystals separated gradually from the solution. This was filtered off, washed first with ice-cold water, then with alcohol and dried over fused calcium chloride in vacuo. (Found : Ni, 30.24 ; N, 24.92 ; NO_2^-, 35.80. $Ni_2[C_2H_4(NH_2)_2]_2(NO_2)_3(OH)$ requires Ni, 30.02 ; N, 24.94 ; NO_2^-, 35.14%).

The substance is red in colour and is insoluble in ethyl alcohol, ether, acetone and chloroform. It is highly insoluble in cold water but is decomposed by hot water and alkalies, forming some nickel hydroxide and a bluish violet solution, presumably containing $[Ni(en)_3]^{2-}$ ion. It is also decomposed as usual by acids, aqueous ammonia and ethylendiamine. It is paramaguetic : $\chi_g = 19.6 \times 10^{-6}$; χ_m (cor.) $= 3924 \times 10^{-6}$; $\mu_B = 3.11$.

Analytical Procedures.—Nickel was estimated gravimetrically as nickel dimethylglyoxime after decomposing the substance with hot sulphuric acid. Nitrogen (total) was estimated by semi-micro combustion, while the nitrite in the ethylenediamine complex was estimated by decomposing the complex by digestion with 0.1*N*-KOH and diluting the filtered solution containing the nitrite to a definite volume and estimating the nitrite in the solution by permanganate method as usual. Ethylenediamine present in the nitrite solution did not interfere with the titration. However, in the case *o*-phenylenediamine or benzylamine complex, this method did not work. Attempts to separate the amines by solvent-extraction were also unsuccessful and, hence, nitrite content of these complexes could not be estimated directly.

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Department of Inorganic and Analytical Chemistry,
Indian Association for the Cultivation of Science,
Jadavpur, Calcutta-32.

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SUBSTITUTED BUTYRO LACTONES. PART I. SYNTHESIS OF γ-(4-ALKOXY-3-XENYL)-BUTYRO LACTONES

By D. K. Genge and J. J. Trivedi

β-(4-Alkoxy-3-xenoyl)-propionic acids have been prepared and reduced by hydrogen in presence of Raney nickel. The resulting hydroxy-acids have been lactonised.

The lactone ring is one of the important structural features of santonin and is responsible for the development of anthelmintic properties (Baldwin, *Brit. J. Pharmacol.*, 1943, **3**, 91). Several substituted phenylbutyro lactones possessing anthelmintic activity have been synthesised (Rosenmund and Schapiro, *Arch. Pharm.*, 1934, **272**, 313 ; Nargund *et al.*, *J. Indian Med. Assoc.*, 1945, **14**, 69, 73).

Carbamates of 2-hydroxydiphenyl show anthelmintic properties (Burger, "Medicinal Chemistry", 1951, p. 925). It was of considerable interest to study compounds having a lactone ring attached to a diphenyl group containing an alkoxy group as a substituent. γ-*p*-alkoxybutyro lactones have been shown to exhibit anthelmintic properties (Trivedi and Nargund, *J. Univ. Bombay*, 1942, **11**, Part III, 127 ; Nargund *et. al.*, *loc. cit.*).

β-(4-Alkoxy-3-xenoyl)-propionic acids required for this purpose were prepared by the method of Fieser and Bradsher (*J. Amer. Chem. Soc.*, 1936, **58**, 1738). These keto-acids were reduced by hydrogen in presence of Raney nickel and the resulting hydroxy-acids were lactonised by heating them with sulphuric acid.

Experimental

4-Alkoxydiphenyls were prepared from 4-hydroxydiphenyl and appropriate alkyl halide in presence of sodium ethoxide in 75-80% yield (Gray *et al.*, *J. Chem. Soc.*, 1955, 1419). Condensation of 4-alkoxydiphenyls with succinic anhydride and the separation of isomers were carried out as described by Fieser and Bradsher (*loc. cit.*). Only β-(4-alkoxy-3-xenoyl)-propionic acids were converted into the lactones.

Reduction of β-(4-Alkoxy-3-xenoyl)-propionic Acids.—β-(4-Alkoxy-3-xenoyl)-propionic acid (4 g.) was dissolved in a pressure bottle in 0.1*N*-KOH (18 c.c.) and diluted to 90 c.c. with distilled water. Raney nickel catalyst (4 g.) was added and after evacuating the bottle, hydrogen was admitted to the mechanically shaken pressure bottle at 20 lbs. pressure. At the end of the reaction (1 hour) the catalyst was filtered, the filtrate acidified with H_2SO_4 (conc., 8 c.c.) and the solution was heated on a water-bath for 1 hour to complete lactonisation of the hydroxy-acid. The product obtained on cooling was kept over saturated solution of sodium bicarbonate to remove acidic impurities. The insoluble lactone was extracted with ether and the ether extract was dried over anhydrous magnesium sulphate. The lactone obtained on removal of the ether was purified by crystallisation or distilled under reduced pressure (yield 35%).

As a check over the catalytic hydrogenation method, ethyl β-(4-methoxy-3-xenoyl)-propionate was reduced to γ-(4-methoxy-3-xenyl)-butyro lactone by aluminium *iso*propoxide as follows.

Ethyl β-(4-methoxy-3-xenoyl)-propionate (0.03*M*) was refluxed with a luminium *iso*propoxide (0.03 *M*) in dry *iso*propyl alcohol (30 c.c.) till the distillate was free from acetone (Adams, "Org. Reactions", Vol. II, p. 196). After removal of *iso*propyl alcohol HCl (dil.) was added and the organic layer separating was refluxed with alcoholic sodium hydroxide (30 c.c., 20% and alcohol 15 c.c.). After distilling off alcohol, the residue was diluted with water and the neutral impurities were removed with ether. The solution was then acidified with H_2SO_4 (dil., 25%) and more of the acid was added so as to bring the concentration of the acid to about 15%. It was heated on a water-bath for 2 hours and the lactone was isolated as described above. The lactone had m.p. 100° and did not depress the m.p. of the lactone obtained by catalytic reduction. The compounds prepared are shown in the tables.

TABLE I

S.No.	Name of the compound.	Mol. formula.	B.P. or M.P.	Found.	Calc.
1	*p*-Ethoxydiphenyl	$C_{14}H_{14}O$	Needles from dilute alcohol; 78°	C:84.7% H: 7.0	84.8% 7.1
2	*p*-*n*-Propoxydiphenyl	$C_{15}H_{16}O$	Do; 68°	C:84.6 H: 7.7	84.9 7.6
3	*p*-*n*-Butoxydiphenyl	$C_{16}H_{18}O$	Do; 80°	C:85.0 H: 8.2	84.9 8.0
4	*p*-*n*-Amyloxydiphenyl	$C_{17}H_{20}O$	Do; 58°	C:85.1 H: 8.6	84.9 8.4

TABLE II

No.	Compounds.	Mol. formula.	B.P. or M.P.	Found.	Calc.
1	Ethyl ester of β-(4-methoxy-3-xenoyl)-propionic acid	$C_{19}H_{20}O_4$	Pale yellow liquid; 207-12°/4 mm; n_D^{28} 1.586	C:72.8% H: 6.7	73.0% 6.4
2	Semicarbazone of (1) acid	$C_{18}H_{19}O_4N_3$	Needles from dilute alcohol; 186°	Equiv. 343.3	341.0
3	β-(4-Ethoxy-4′-xenoyl)-propionic acid	$C_{18}H_{18}O_4$	Granules from acetic acid; 180°	C:72.4 H: 6.3 Equiv. 300.5	72.5 6.0 298.0
4	β-(4-Ethoxy-3-xenoyl)-propionic acid	$C_{18}H_{18}O_4$	Granules from dilute alcohol; 165°	C.72.2 H: 6.2 Equiv. 296.2	72.5 6.0 298.0
5	Ethyl ester of (4)	$C_{20}H_{22}O_4$	Pale yellow liquid; 235-40°/8 mm; n_D^{22} 1.598	C:73.3 H: 2.8	73.6 3.0
6	Semicarbazone of (4)	$C_{19}H_{21}O_4N_3$	Needles from dilute alcohol; 240°	Equiv. 354.0	355.0
7	β-(4-*n*-Propoxy-4′-xenoyl)-propionic acid	$C_{19}H_{20}O_4$	Needles from acetic acid; 192°	C:73.0 H: 6.7 Equiv. 313.	73.1 6.4 312.0

TABLE II (contd.)

S No.	Compounds.	Mol. formula.	B.P. or M.P.	Found.	Calc.
8	β-(4-*n*-Propoxy-3-xenoyl)-propionic acid	$C_{19}H_{20}O_4$	Small needles from hot water; 154°	C: 72.9% H: 6.6 Equiv. 314.4	73.1% 6.4 312.0
9	Ethyl ester of (8)	$C_{21}H_{24}O_4$	Pale yellow liquid; 243-47°/5 mm; n_D^{28} 1.588	C: 74.4 H: 7.3	74.1 7.0
10	Semicarbazone of (8)	$C_{20}H_{23}O_4N_3$	Needles from dil. alcohol; 184°	Equiv. 371.4	369.0
11	β-(4-*n*-Butoxy-4′-xenoyl)-propionic acid	$C_{20}H_{22}O_4$	Needles from acetic acid; 218°	C: 73.2 H: 6.5 Equiv. 328.0	73.5 6.7 326.0
12	β-(4-*n*-Butoxy-3-xenoyl)-propionic acid	$C_{20}H_{22}O_4$	Needles from ethyl acetate and petroleum ether; 154°	C: 73.5 H: 6.6 Equiv. 324.2	73.6 6.7 326.0
13	Ethyl ester of (12)	$C_{22}H_{26}O_4$	Pale yellow liquid; 250-55°/10 mm; n_D^{28} 1.588	C: 74.3 H: 7.5	74.6 7.3
14	Semicarbazone of (12)	$C_{21}H_{25}O_4N_3$	Needles from dil. alcohol; 214°	Equiv. 386.3	383.0
15	β-(4-*n*-Amyloxy-4′-xenoyl)-propionic acid	$C_{21}H_{24}O_4$	Needles from acetic acid; 197°	C: 74.3 H: 7.3 Equiv. 337.6	74.1 7.3 340.0
16	β-(4-*n*-Amyloxy-3-xenoyl)-propionic acid	$C_{21}H_{24}O_4$	Needles from dil. alcohol; 185°	C: 74.3 H: 7.3 Equiv. 342.7	74.1 7.0 340.0
17	Ethyl ester of (16)	$C_{23}H_{28}O_4$	Pale yellow liquid; 268-73°/8 mm; n_D^{28} 1.574	C: 76.5 H: 7.8	76.8 7.6
18	Semicarbazone of (16)	$C_{22}H_{27}O_4N_3$	Needles from dil. alcohol; 254°	Equiv. 395.3	397.0

TABLE III

S. No.	Compounds.	Mol. formula.	M.P. or B.P.	Found.	Calc.
1	γ-(4-Methoxy-3-xenyl)-butyro lactone.	$C_{17}H_{16}O_3$	Granules from benzene-petrol; 100°	C: 76.1% H: 6.2 Equiv. 270.1	76.1% 6.0 268.0
2	γ-(4-Ethoxy-3-xenyl)-butyro lactone.	$C_{18}H_{18}O_3$	Distilled at 125°/2 mm. (oil-bath); 130°	C: 76.5 H: 6.5 Equiv. 280.2	76.6 6.4 282.0
3	γ-(4-*n*-Propoxy-3-xenyl)-butyro lactone	$C_{19}H_{20}O_3$	Do; 124°	C: 77.2 H: 6.6 Equiv. 296.5	77.0 6.8 296.0
4	γ-(4-*n*-Butoxy-3-xenyl)-butyro lactone.	$C_{20}H_{22}O_3$	Do; 137°	C: 77.6 H: 7.2 Equiv. 307.9	77.4 7.1 310.0
5	γ-(4-*n*-Amyloxy-3-xenyl)-butyro lactone.	$C_{21}H_{24}O_3$	Do; 134°	C: 77.5 H: 7.6 Equiv. 322.2	77.8 7.4 324.0

L. D. ARTS COLLEGE,
AND M. R. SCIENCE INSTITUTE,
AHMEDABAD.

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SUBSTITUTED BUTYRO LACTONES. PART II. SYNTHESIS OF γ-(2-ALKOXY-5-BENZYLPHENYL)-BUTYRO LACTONES

By D. K. Genge and J. J. Trivedi

β (2-Alkoxy-5-benzylbenzoyl)-propionic acids have been prepared and reduced The resulting hydroxy-acids have been lactonised by heating with dilute sulphuric acid.

The importance of a lactone ring and an alkoxy group in the development of anthelmintic properties has been set forth in the previous paper (this *issue*, p. 801). Carbamate of 4-hydroxydiphenylmethane shows anthelmintic properties and is used in medicine in the treatment of oxyuriasis (Francke, *Med. Klin*, 1920, **16**, 758). Schulemann (*Deut. Med. Wochenschr.*, 1920, **46**, 1051) has reported the anthelmintic properties of 2- and 4-benzylphenols and 4-phenyl-3-methylphenol. It was therefore felt of interest to study the compounds having a lactone ring attached to 4-alkoxydiphenylmethane.

β-(2-Alkoxy-5-benzylbenzoyl)-propionic acids required for this purpose were prepared by the method of Burtner and Brown (*J. Amer. Chem. Soc.*, 1953, **75**, 2334). These keto-acids were reduced by hydrogen in presence of Raney nickel and the resulting hydroxy-acids were lactonised by heating with dilute sulphuric acid.

Experimental

4-Hydroxydiphenylmethane was prepared from phenol and benzyl chloride by the method of Short and Stewart (*J. Chem. Soc.*, 1929, 555). 4-Alkoxydiphenylmethanes were prepared from 4-hydroxydiphenylmethane and the appropriate alkyl halide in presence of sodium ethoxide in 75-80% yield. Condensation of 4-alkoxydiphenylmethane with succinic anhydride was carried out as described by Burtner and Brown (*loc. cit.*) in the case of 4-methoxydiphenylmethane. The constitutions of these acids have been assumed to be β-(2-alkoxy-5-benzylbenzoyl)-propionic acid by analogy with β-(2-methoxy-5-benzylbenzoyl)-propionic acid.

Reduction of β-(2-Alkoxy-5-benzylbenzoyl)-propionic acids was carried out as described in the previous paper in the case of β-(4-alkoxy-3-xenoyl)-propionic acids (*loc. cit.*). Lactones were purified by keeping them over potassium carbonate for 24 hours (yield 45%). These were characterised by the preparation of hydroxy-acids or *S*-benzyl*iso*thiuronium salts. The compounds are described in Tables I—III.

TABLE I

Sl. No.	Diphenylmethanes.	Formula.	Appearance, b.p. or m.p. and ref. index.	Found.	Calc.
1	4-*n*-Propoxy-	$C_{16}H_{18}O$	Pale yellow liquid; 168-73°/3mm; n_D^{40} 1.549	C: 85.1% H: 8.2	84.9% 8.0
2	4-*n*-Butoxy-	$C_{17}H_{20}O$	Do; 178-83°/8mm; n_D^{40} 1.548	C: 85.1 H: 8.6	84.9 8.4
3	4-*n*-Amyloxy-	$C_{18}H_{22}O$	Do; 178-83°/3mm; n_D^{40} 1.545	C: 84.8 H: 8.9	85.0 8.7
4	4-*n*-Hexyloxy-	$C_{19}H_{24}O$	Do; 233-35°/28mm; n_D^{40} 1.543	C: 85.2 H: 9.2	85.0 9.0

TABLE II

Sl. No.	Compounds.	Formula.	Appearance, b.p. or m.p. and ref. index.	Found.	Calc.
1	Ethyl ester of β-(2-methoxy-5-benzylbenzoyl)-propionic acid	$C_{20}H_{22}O_4$	Pale yellow liquid; 257-62°/5mm; n_D^{38} 1.559	C: 73.7% H: 6.9	73.6% 6.7
2	Semicarbazone of β-(2-methoxy-5-benzylbenzoyl)-propionic acid	$C_{19}H_{21}O_4N_3$	Needles from alcohol; 159°	Equiv. 357.3	355.0
3	β-(2-Ethoxy-5 benzyl-benzoyl)-propionic acid	$C_{19}H_{20}O_4$	Needles from benzene-petrol; 140°	C: 73.2 H: 6.7 Equiv. 314.5	73.0 6.4 312.0
4	Ethyl ester of (3)	$C_{21}H_{24}O_4$	Pale yellow liquid; 223-28°/6mm; n_D^{38} 1.556	C: 74.3 H: 7.2	74.1 7.0
5	Semicarbazone of (3)	$C_{20}H_{23}O_4N_3$	Needles from dilute alcohol; 183°.	Equiv. 370.9	369.0
6	β-(2-*n*-Propoxy-5-benzyl-benzoyl)-propionic acid	$C_{20}H_{22}O_4$	Cluster of needles from benzene-petrol; 118°.	C: 73.4 H: 6.8 Equiv. 327.6	73.6 6.7 326.0
7	Ethyl ester of (6)	$C_{22}H_{26}O_4$	Pale yellow liquid; 253-56°/4mm; n_D^{38} 1.532	C: 74.7 H: 7.6	74.6 7.3
8	Semicarbazone of (6)	$C_{21}H_{25}O_4N_3$	Needles from dilute alcohol; 158°.	Equiv. 381.2	383.0
9	β-(*n*-Butoxy-5-benzyl-benzoyl)-propionic acid	$C_{21}H_{24}O_4$	Needles from benzene-petrol; 119°.	C: 73.9 H: 7.1 Equiv. 338.1	74.1 7.0 340.0
10	Ethyl ester of (9)	$C_{23}H_{28}O_4$	Pale yellow liquid; 263-68°/4mm; n_D^{38} 1.545	C: 75.2 H: 7.5	75.0 7.6
11	Semicarbazone of (9)	$C_{22}H_{27}O_4N_3$	Needles from dilute alcohol; 144°.	Equiv. 396.0	397.0
12	β-(2-*n*-Amyloxy-5-benzyl-benzoyl)-propionic acid	$C_{22}H_{26}O_4$	Needles from benzene-petrol; 124°.	C: 74.3 H: 7.5 Equiv. 355.0	74.6 7.3 354.0
13	Ethyl ester of (12)	$C_{24}H_{30}O_4$	Pale yellow liquid; 203-208°/4mm; n_D^{38} 1.534	C: 75.5 H: 8.0	75.4 7.9
14	Semicarbazone of (12)	$C_{23}H_{29}O_4N_3$	Needles from dilute alcohol; 174°.	Equiv. 413.3	411.0
15	β-(2-*n*-Hexyloxy-5-benzyl-benzoyl)-propionic acid	$C_{23}H_{28}O_4$	Needles from benzene-petrol; 130°.	C: 75.2 H: 7.8 Equiv. 369.4	75.0 7.6 368.0
16	Ethyl ester of (15)	$C_{25}H_{32}O_4$	Pale yellow liquid; 257-62°/8mm; n_D^{38} 1.535	C: 75.5 H: 8.3	75.7 8.1
17	Semicarbazone of (15)	$C_{24}H_{31}O_4N_3$	Needles from dilute alcohol; 165°	Equiv. 424.0	425.0

TABLE III

S. No.	Compounds.	Fomula.	Appearance, b.p. or m.p. and ref. index.	Found.	Calc.
1	γ-(2-Methoxy-5-benzylphenyl)-butyro lactone	$C_{18}H_{18}O_3$	Granules from benzene-petrol; 105°	C: 76.3% H: 6.5 Equiv. 280.5	76.6% 6.4 282.0
2	γ-(2-Methoxy-5-benzylphenyl)-γ-hydroxybutyric acid	$C_{18}H_{20}O_4$	Needles from benzene-petrol; 128°	C: 71.9 H: 6.8 Equiv. 301.8	72.0 6.7 300.0
3	*S*-Benzyl*iso*thiuronium salt of (2)	$C_{26}H_{30}O_4N_2S$	121°	S: 6.9	6.9
4	γ-(2-Ethoxy-5-benzylphenyl)-butyro lactone	$C_{19}H_{20}O_3$	Pale yellow liquid; 268-73/4mm; n_D^{40} 1.574	C: 77.2 H: 6.8 Equiv. 298.7	77.0 6.7 296.0
5	γ-(2-Ethoxy-5-benzylphenyl)-γ-hydroxybutyric acid	$C_{19}H_{22}O_4$	120°	C: 72.4 H: 7.3 Equiv. 317.0	72.6 7.0 314.0
6	*S*-Benzyl*iso*thiuronium salt of (5)	$C_{27}H_{32}O_4N_2S$	124°	S: 6.8	6.7
7	γ-(2-*n*-Propoxy-5-benzylphenyl)-butyro lactone	$C_{20}H_{22}O_3$	Pale yellow liquid; 237-42°/4mm; n_D^{40} 1.560	C: 77.0 H: 7.2 Equiv. 311.4	77.2 7.1 310.0
8	γ-(2-*n*-Propoxy-5-benzylphenyl)-γ-hydroxybutyric acid	$C_{20}H_{24}O_4$	102°	C: 72.9 H: 7.5 Equiv. 330.1	73.1 7.3 328.0
9	*S*-Benzyl*iso*thiuronium salt of (8)	$C_{28}H_{34}O_4N_2S$	126°	S: 6.7	6.5
10	γ-(2-*n*-Butoxy-5-benzylphenyl)-butyro lactone	$C_{21}H_{24}O_3$	Pale yellow liquid, 257-62°/3mm; n_D^{40} 1.560	C: 77.5 H: 7.7 Equiv. 322.3	77.8 7.4 324.0
11	γ-(2-*n*-Butoxy-5-benzylphenyl)-γ-hydroxybutyric acid	$C_{21}H_{26}O_4$	90°	C: 73.7 H: 7.8 Equiv. 343.0	73.7 7.6 342.9
12	*S*-Benzyl*iso*thiuronium salt of (11)	$C_{29}H_{38}O_4N_2S$	124°	S: 6.4	6.3
13	γ-(2-*n*-Amyloxy-5-benzylphenyl)-butyro lactone	$C_{22}H_{26}O_3$	Pale yellow liquid; 233-38°/3mm; n_D^{40} 1.555	C: 77.9 H: 7.8 Equiv. 338.5	78.1 7.7 338.0
14	γ-(2-*n*-Hexyloxy-5-benzylphenyl)-butyro lactone	$C_{23}H_{28}O_3$	Pale yellow liquid, 298-303°/10 mm; n_D^{40} 1.567	C: 78.6 H: 8.2 Equiv. 354.2	78.4 8.0 352.0

L. D. ARTS COLLEGE
AND M. R. SCIENCE INSTITUTE,
AHMEDABAD.

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STUDIES IN COMPLEX FORMATION WITH COLLOIDAL MERCURISULPHOSALICYLIC ACID. PART II. COMPLEX ALUMINIUM MERCURISULPHOSALICYLATE

By Rajendra S. Singh and Satya Prakash

Colloidal mercurisulphosalicylic acid, possessing co-ordinating groups similar to sulphosalicylic acid, forms similar complexes with aluminium. Potentiometric and conductometric studies show that it forms two types of complexes: (*a*) 1 :1 complex in acidic medium when the ratio of the metal to acid is less than 1 :2, and (*b*) 1 :2 complex when the ratio is 1 :2 or more. The 1 :2 complex is stable as the aluminium is not precipitated on addition of alkali. In both the complexes the phenolic hydrogen is displaced during complex formation and the co-ordination takes place between the oxygen atoms of phenolic and carboxyl groups.

In Part I of this series (this *Journal*, 1957, **34**, 197), the authors have reported the study of complex formation between beryllium and mercurisulphosalicylate. In this paper the physico-chemical studies on the formation of aluminium mercurisulphosalicylate in solution have been reported.

Aluminium is known to form complexes with sulphosalicylic, sulphobenzoic and sulphohydroxynaphthoic acids (Dominikiewiez, *Arch. Chem. Farm.*, 1934, **1**, 92). Babko (*J. Gen. Chem.*, U.S.S.R., 1948, **18**, 1617) has reported the formation of aluminium salicylate complexes. Anderson and Lasater (*J. Amer. Chem. Soc.*, 1952, **74**, 1429) studied the complex aluminium sulphosalicylate spectrophotometrically, using copper sulphosalicylate complex as an indicator.

Experimental

The experimental procedure adopted in this paper was the same as followed in the previous part (*loc. cit.*). Solutions of mercurisulphosalicylic acid and potassium chloromercurisulphosalicylate were prepared as described therein.

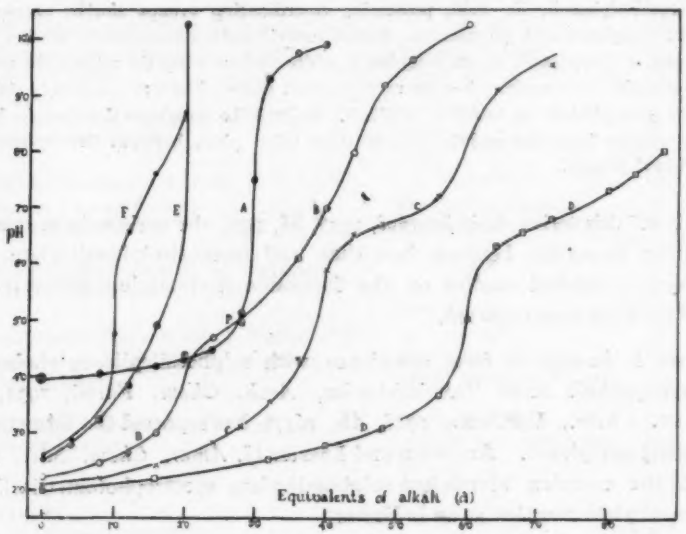
Solutions of aluminium chloride were prepared by diluting a stock solution of $AlCl_3.6H_2O$ (Baker's analysed), the aluminium content of which was estimated gravimetrically as $Al(C_9H_6CN)_3$ with 8-hydroxyquinoline (oxine) (Vogel, "Text Book of Quantitative Inorganic Analysis", London, 1951, p. 372).

The specific conductivity and p_H measurements were made at a constant temperature of $32° \pm 0.1°$.

Discussion

Figure 1 represents the changes in the p_H that take place when aluminium chloride, potassium chloromercurisulphosalicylate and their mixtures are titrated with alkali. The abscissa represents the number of equivalents of alkali (a) per gram ion of aluminium. Curve A is for $6.25 \times 10^{-3}M$-$AlCl_3$ and the curves B to D are for 1 : 1 (Curve B), 1 : 2 (Curve C) and 1 : 4 mixtures (Curve D) of aluminium chloride and potassium chloromercurisulphosalicylate of the same concentrations. Curves E and F are for $6.25 \times 10^{-3}M$ solution of mercurisulphosalicylate and potassium chloromercurisulphosalicylate respectively and are recorded for comparison.

Fig. 1



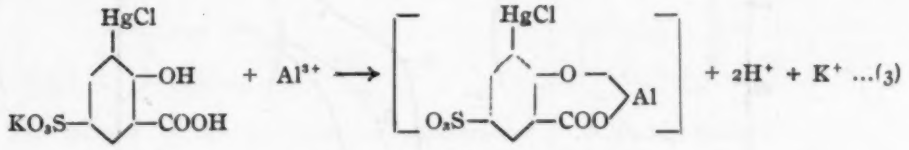
From Fig. 1 it may be noted that the precipitation of aluminium hydroxide starts at p_H 5.12 (Curve A), when nearly three equivalents of alkali have been added. At p_H 10.0, when four equivalents of alkali have been added, the precipitate of aluminium hydroxide dissolves to form sodium aluminate.

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \quad \ldots \quad \ldots \quad (1)$$

$$Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O \quad \ldots \quad \ldots \quad (2)$$

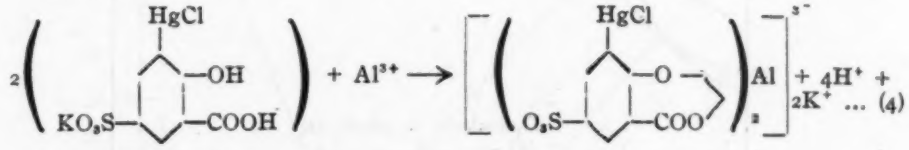
The neutralisation of mercurisulphosalicylate and potassium chloromercurisulphosalicylate has been discussed in an earlier publication (*loc. cit.*).

The 1 : 1 mixture of aluminium chloride and potassium chloromercurisulphosalicylate (Curve B) has an initial p_H (2.25) which is lower than both of aluminium chloride (3.70) and potassium chloromercuri salt (2.60) alone. The curve has an inflection at $a=2$, which indicates the formation of a complex according to :



A crystalline white precipitate is obtained at p_H 4.70 and above, the quantity, however, decreases with an increase in p_H, and at p_H 9.65 no precipitate is obtained. The exact nature of the precipitate has not been investigated, but it may be some hydrolysis product of the complex formed.

The 1 : 2 and 1 : 4 mixtures of aluminium and potassium chloromercurisulphosalicylate (Curves C & D) have again an initial p_H which is lower than both that of aluminium chloride or potassium chloromercurisulphosalicylate alone. Both the curves show an inflection at $a=4$ and 6 respectively, which clearly indicates that two moles of potassium chloromercurisulphosalicylate react with one mole of aluminium to form a complex.

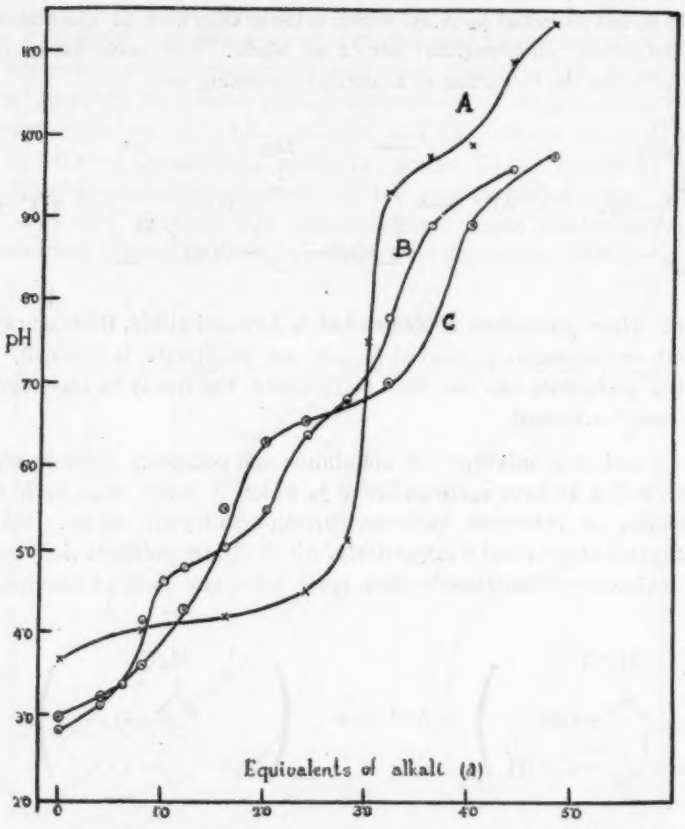


No crystalline white precipitate is obtained in both the mixtures as obtained in 1 : 1 mixture, showing the stability of the complex formed.

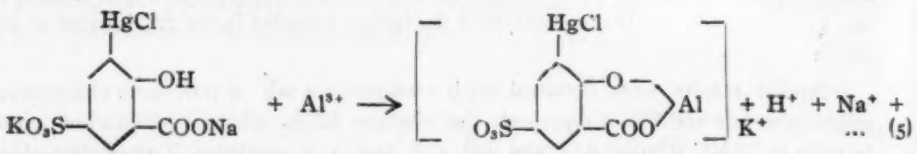
From these facts it is clear that potassium chloromercurisulphosalicylate forms two types of complexes with aluminium(III) : (a) 1 : 2 complex when the ratio of aluminium to potassium chloromercurisulphosalicylate is two or more and (b) 1 : 1 complex when the ratio is one or more but less than two. The 1 : 2 complex is more stable than the 1 : 1 complex, as the aluminium of the former complex is not precipitated at all by alkali.

Similar results were obtained with monosodium salt of potassium chloromercurisulphosalicylate and Fig. 2 represents the changes in p_H when (*i*) aluminium chloride (3.125×10^{-3} *M*) (Curve A), and (*ii*) 1 : 1 and 1 : 4 mixtures of aluminium chloride (3.125×10^{-3} *M*) and monosodium salt (3.125×10^{-3} *M*) (Curves B & C) are titrated with alkali respectively. The abscissa represents the number of equivalents of alkali added. The addition of alkali to aluminium chloride has already been discussed (vide equation 1).

FIG. 2



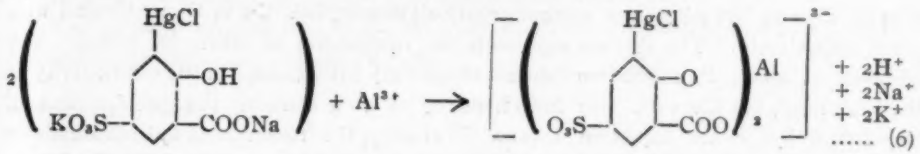
The 1 : 1 mixture of monosodium potassium chloromercurisulphosalicylate and aluminium chloride (III) (Curve B) has an initial p_H (2.85) which is lower than both of aluminium chloride (3.98) and the monosodium salt (6.20) alone, which shows an increase in the hydrogen-ion concentration of the mixture. There is an inflection at one equivalent of the alkali in the p_H curve. This indicates the formation of a complex according to the equation :



A crystalline white precipitate is obtained at p_H range 4.80–6.40, above which no precipitate is obtained.

The 1 : 4 mixture (Curve C) has also an initial p_H which is lower than both of aluminium and monosodium salt alone, but an inflection in the curve occurs at about

$a=2$. No precipitation is observed which shows the greater stability of the complex formed. The inflection at $a=2$ shows that two moles of potassium chloromercurisul phosalicylate combine with aluminium to form a complex, the co-ordination taking place between the oxygen atoms of hydroxyl and carboxyl groups.



..... (6)

The increase in the hydrogen-ion concentration of the mixture shows clearly that the hydroxyl hydrogen is displaced during complex formation.

FIG. 3

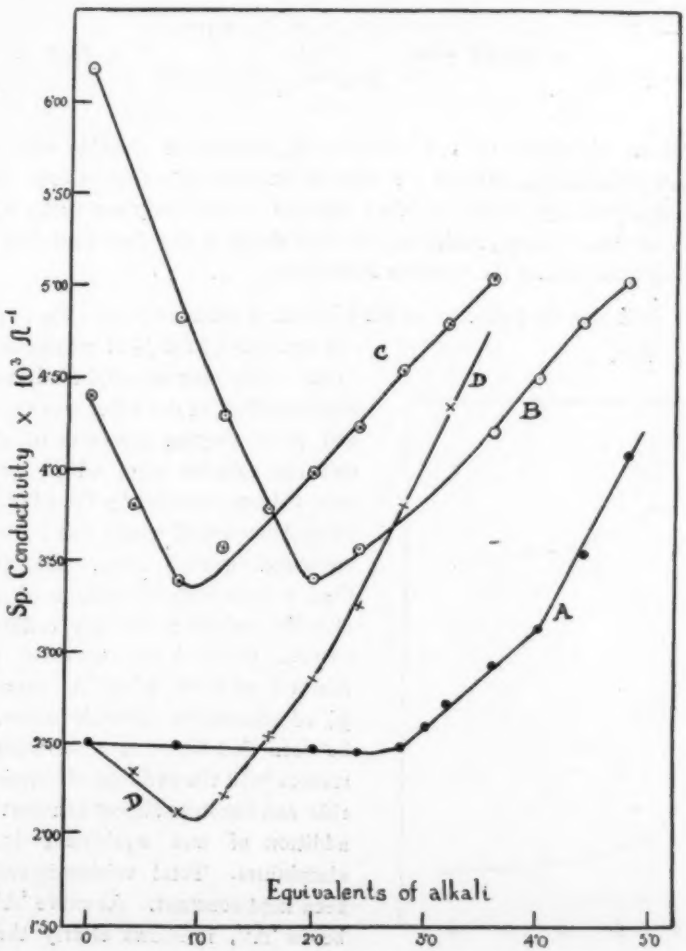
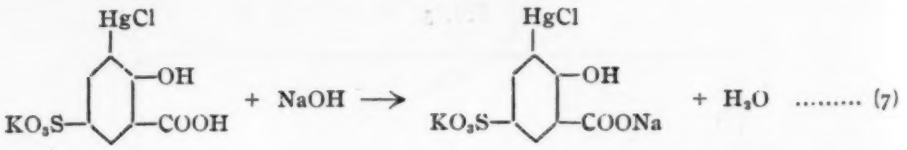


Fig. 3 represents the changes in specific conductivity when (*i*) (6.25×10^{-3} *M*) aluminium chloride (Curve A), (*ii*) 1 : 1 mixture of (6.25×10^{-3} *M*) potassium chloromercurisulphosalicylate (Curve B), (*iii*) 1 : 1 mixture of (6.25×10^{-3} *M*) aluminium chloride and (6.25×10^{-3} *M*) monosodium potassium chloromercurisulphosalicylate (Curve C) and (*iv*) potassium chloromercurisulphosalicylate (Curve D) are titrated with alkali respectively. The abscissa represents the equivalents of alkali (*a*) added. The addition of alkali to aluminium chloride shows very little change in the conductivity in the beginning, but there are two inflections : (*i*) at $a=4$ showing the precipitation of aluminium hydroxide (equation 1) and (*ii*) at $a=3$, the formation of sodium aluminate (equation 2). The addition of alkali to potassium chloromercurisulphosalicylate to (D) shows alminimum at $a=1$, according to the reaction :

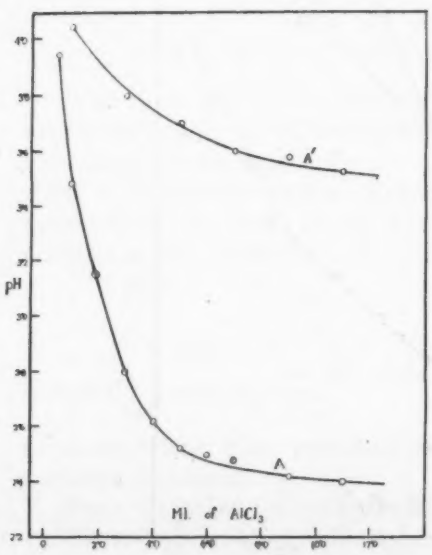


..... (7)

The addition of alkali to 1 : 1 mixture of aluminium chloride with potassium chloromercurisulphosalicylate (B) and its monosodium salt (C) respectively shows minima in the conductivity curves at $a=2$ and $a=1$ respectively according to reactions (3) and (5). The observations provide an added evidence to the fact that the hydroxyl hydrogen is displaced during the complex formation.

Figure 4 indicates the influence of the addition of aluminium chloride in the increased quantity of the p_H of monosodium potassium chloromercurisulphosalicylate. The concentration on the latter was kept constant and to it varying amounts of aluminium chloride solution were added keeping the total volume constant by the addition of calculated amount of water, and p_H values were measured in each case. The abscissa in Fig. 4 represents the volume of aluminium chloride solution and the ordinate, the p_H values. Curve A represents the p_H of the mixture solution, while 'A'' represents the p_H of aluminium chloride alone. It will be seen that the p_H of monosodium salt decreases with the addition of aluminium chloride and becomes almost constant after the addition of one equivalent (5.0 c.c.) of aluminium. Total volume in each case had been kept constant. As curve 'A' lies much below 'A'', it shows clearly that there is

FIG. 4



an increase in the hydrogen-ion concentration of monosodium potassium chloromercurisulphosalicylate on the addition of aluminium ions. This can only be explained to be due to the displacement of the phenolic hydrogen, which takes place during complex formation. The reaction may be represented by equation (5).

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CHEMICAL LABORATORIES,
UNIVERSITY OF ALLAHABAD,
ALLAHABAD.

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PREPARATION OF SOME 5-SUBSTITUTED 2-ARYLIMINO-4-THIAZOLIDONES

By B. K. Patnaik and H. K. Pujari

Ten 5-sulphonamidophenyl-, four 5-phenyl-, and three 5-sulphophenyl-2-arylimino-4-thiazolidones have been prepared by utilising the reaction first reported by Mohlau and Berger.

In view of the fact that 3-ethylthiazoline-2-sulphanilamide has been reported to possess powerful growth inhibiting action of *Mycobacterium tuberculosis* (*J. Pharm. Soc. Japan*, 1952, **72**, 16), it is considered of interest to synthesise some new types of sulphonamido derivatives of thiazolidones.

The experimental procedure adopted in the present investigation is based on the observation of Mohlau and Berger (*Ber.*, 1893, **26**, 1994) and Kuhling (*Ber.*, 1895, **28**, 41, 523) that by the decomposition of a diazo compound, the organic radical formed stabilises itself by becoming attached to another carbon atom. The thiazolidone compounds prepared by the method of Rout and Mohapatra (*J. Amer. Chem. Soc.*, 1955, **77**, 2427) were coupled with diazotised sulphanilamide, employing conditions under which the diazo compounds formed were quickly decomposed with splitting of nitrogen, yielding the desired compounds. After decomposition of the diazo compound, it has been assumed that the sulphonamidophenyl group is attached to the $\cdot CH_2$ group in 5-position of the thiazolidone nucleus, in support of which the evidences discussed by Rout and Patnaik (this *Journal*, 1955, **32**, 563) may be advanced.

Three 5-sulphophenyl- and four 5-phenyl-2-arylimino-4-thiazolidones have also been prepared by following the above method.

Experimental

5-Sulphonamidophenyl-2-p-tolylimino-4-thiazolidone.—Diazotised sulphanilamide, prepared by diazotising sulphanilamide (2.1 g.), was added to a solution, placed in an ice-bath, of 2-*p*-tolylimino-4-thiazolidone (2.5 g.) in a mixture of acetone (50 c.c.) and alcohol (10 c.c.) containing suspended crystalline sodium acetate (6 g.). A solution of cupric chloride (4 g. in 20 c.c. water) was then added dropwise during 3 to 4 hours and the whole warmed gently on a water-bath with stirring at 45° until gas evolution had ceased. The reaction mixture was then allowed to settle, the supernatant liquid decanted off and the precipitate was agitated with acetone (30 c.c.) to remove any unchanged thiazolidone. The precipitate was then collected, dried in air and finally recrystallised from alcohol in grey needles, m.p. 185°, yield 66%. (Found: N, 11.26; S, 17.22. $C_{16}H_{16}O_3N_3S_2$ requires N, 11.63; S, 17.73%).

The properties of other 5-sulphonamidophenyl-2-arylimino-4-thiazolidones are described in Table I.

TABLE I

No.	Aryl group.	Yield.	M.P.	Cryst. form.	% Nitrogen. Found.	% Nitrogen. Calc.	% Sulphur. Found	% Sulphur. Calc.
1	*o*-Tolyl	60%	175°	Brown plates	11.23	11.63	17.51	17.73
2	*p*-Tolyl	60	185°	Grey needles	11.26	11.63	17.22	17.73
3	*o*-Chlorophenyl	55	145°	Yellow ,,	10.92	11.01	16.34	16.78
4	*m*-Chlorophenyl	50	>300°	Pale yellow flakes	10.64	11.01	16.40	16.78
5	*m*-Nitrophenyl	50	105°	Dark brown needles	10.12	10.11	15.92	16.32
6	*p*-Nitrophenyl	55	>300°	Yellow ,,	10.27	10.71	15.86	16.32
7	*o*-Carboxyphenyl	60	130°	Grey ,,	10.28	10.74	16.13	16.37
8	*m*-Carboxyphenyl	55	210°	Grey flakes	10.36	10.74	16.24	16.37
9	*p*-Carboxyphenyl	63	217°	Grey needles	10.45	10.74	16.14	16.37
10	α-Naphthyl	60	160°	Brown ,,	8.38	8.88	13.14	13.53

5-Sulphophenyl-2-phenylimino-4-thiazolidone.—Diazotised sulphanilic acid, prepared by diazotising sulphanilic acid (2.1 g.), was added to an ice-cold solution of 2-phenylimino-4-thiazolidone (2.34 g.) in acetone (50 c.c.) in which crystallised sodium acetate (6 g.) was suspended. A solution of cupric chloride (4 g. in 20 c.c. water) was added to it dropwise with constant stirring, and the whole warmed on a water-bath. The product separating as a buff-coloured copper salt was allowed to settle, the supernatant liquid decanted off and the precipitate agitated with acetone (30 c.c.). The precipitate, after being air-dried, was digested with NaOH solution (2*N*) in which it dissolved, the copper content, however, being precipitated. After filtration the alkaline solution was acidified with HCl, furnishing the final product as light brown crystals, m.p. 225°, yield 63%. (Found: S, 17.94. $C_{15}H_{12}O_4N_2S_2$ requires S, 18.39%). The properties of other 5-sulphophenyl-2-arylimino-4-thiazolidones are described in Table II.

TABLE II

No.	Aryl group.	Yield.	M.P.	Cryst. form	% Sulphur. Found.	% Sulphur. Calc.
1	Phenyl	63%	226°	Light brown needles	17.94	18.39
2	*p*-Nitrophenyl	56	207°	Yellowish brown needles	15.83	16.28
3	β-Naphthyl	68	93°	Brown needles	15.67	16.08

5-Phenyl-2-phenylimino-4-thiazolidone.—Diazotised aniline was treated with 2-phenylimino-4-thiazolidone in acetone in presence of crystallised sodium acetate as described above. The product was then decomposed by adding a solution of cupric chloride and the product was isolated in the manner described earlier which separated as light yellow needles, m.p. 154°, yield 68%. (Found: S, 11.63. $C_{15}H_{12}ON_2S$ requires S, 11.94%).

The properties of other 5-phenyl-2-phenylimino-4-thiazolidones are described in Table III.

TABLE III

No.	Aryl group.	Yield.	M.P.	Cryst. form	% Sulphur. Found.	Calc.
1	Phenyl	68%	154°	Yellow needles	11.63	11.94
2	*m*-Chlorophenyl	65	161°	Yellow flakes	10.12	10.56
3	*p*-Chlorophenyl	64	267°	Yellow needles	10.24	10.56
4	*p*-Nitrophenyl	73	216°	Brown ,,	9.85	10.22

The authors express their sincere thanks to Dr. M. K. Rout, Reader in Chemistry, Ravenshaw College, Cuttack, for suggesting the problem and for his guidance and to the Board of Scientific and Industrial Research for research grants to carry out this investigation.

MAYURBHANJ CHEMICAL LABORATORY,
RAVENSHAW COLLEGE,
CUTTACK-3.

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BROMINATION OF ETHYL β-ARYLAMINOMETHYLENE -CYANOACETATES, -ACETOACETATES AND -MALONATES

By H. D. Upadhyaya and C. M. Desai

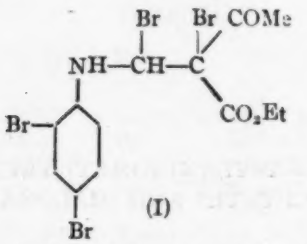
Bromination of ethyl β-anilinomethylene-cyanoacetate, -acetoacetate and -malonate has been investigated in chloroform and acetic acid in different proportions. The αβ-dibromo derivative of ethyl β-anilinomethylene-cyanoacetate has been found to be more stable than that of the acetoacetate, while the corresponding malonate derivative seems to be highly unstable. Ethyl β-anilinomethylene-acetoacetate and -malonate are decomposed during bromination in chloroform.

It was shown by Dains and Griffin (*J. Amer. Chem. Soc.*, 1911, **33**, 963) that the monobromo product obtained by Dains (*Ber.*, 1902, **35**, 2510) by bromination of ethyl β-anilinomethylene-cyanoacetate in glacial acetic acid was ethyl α-cyano-β-*p*-bromo-anilinoacrylate. Dains, O' Brien and Johnson (*J. Amer. Chem. Soc.*, 1916, **38**, 1510) suggested that the aminomethylene compounds containing the grouping $>C:CH.NHR$ reacted also in the tautomeric form $>CH.CH:NR$. The dibromide obtained from the latter form may under the influence of solvents either lose its bromine entirely or undergo rearrangement, yielding a monobromo-substitution product and hydrogen bromide.

Bromination of ethyl β-arylaminomethylene-acetoacetates and -malonates and ethyl β-arylamino-β-carbethoxyacrylates in chloroform was found, with excess of bromine, to yield αβ derivatives containing two or three bromine atoms in the nucleus (Mapara and Desai, this *Journal*, 1955, **32**, 52). Chlorination of ethyl β-arylamino-methylene-malonates in chloroform by sulphuryl chloride was reported to furnish products having chlorine both in the nucleus and in the side chain (Upadhyaya and Desai, *Science & Culture*, 1955, **21**, 37). But further work revealed that the products, thus obtained, were hydrobromides or hydrochlorides of the corresponding haloamines.

So the bromination of these esters was investigated further by varying (*a*) the proportion of bromine, (*b*) the solvent and (*c*) the concentration of the ester in the solvent employed. This investigation has brought to light the following facts:

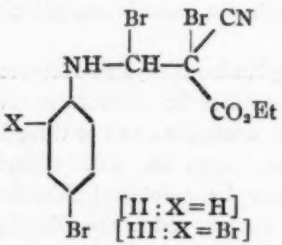
(*i*) Bromination of ethyl β-anilinomethylene-cyanoacetate in chloroform affords the αβ-dibromo derivative, whereas the bromination of the corresponding acetoacetate and malonate in chloroform leads to decomposition and formation of the hydrobromides of the bromoamines (cf. Mapara and Desai, *loc. cit.*). Further, bromination of the cyanoacetate with an equimolecular quantity of bromine furnishes ethyl β-*p*-bromo-anilinomethylene-cyanoacetate, whereas under the same conditions, the acetoacetate affords a small quantity of ethyl αβ-dibromo-β-*op*-dibromoanilinomethylene-aceto-acetate (I).



(I)

(*ii*) The side-chain brominated derivatives of all the above esters are unstable and lose their side-chain bromine slowly on exposure, but rapidly on treatment with water. Such a derivative of ethyl β-anilinomethylene-cyanoacetate is, however, less unstable than that of the corresponding acetoacetate, whereas the corresponding malonate derivative is highly unstable and, hence, could not be investigated.

(*iii*) The amount of solvent and the reaction time are important factors, as their variations determine the nature of the products obtained. Thus, when ethyl β-anilinomethylene-cyanoacetate is treated with two or three moles of bromine in a large volume of chloroform or acetic acid, ethyl αβ-dibromo-β-*p*-bromoanilinomethylene-cyanoacetate (II) is obtained ; when, however, the bromination is carried out with excess of bromine in the minimum possible volume of the solvent, ethyl αβ-dibromo-β-*op*-dibromoanilinomethylene-cyanoacetate (III) is produced. If the reaction mixture is allowed to stand for a very long time, the side chain begins to decompose and a small quantity of *sym*.-tribromoaniline hydrobromide is precipitated.



[II : X = H]
[III : X = Br]

(*iv*) All attempts to prepare ethyl αβ-dibromo-β-*sym*.-tribromoanilinomethylene-cyanoacetate or the corresponding product without the side-chain bromine failed.

(*v*) Ethyl β-*m*-nitroanilinomethylene-malonate could not be brominated even in glacial acetic acid without rupture of the side chain, and so 3-nitro-6-bromoaniline hydrobromide was obtained.

EXPERIMENTAL

Ethyl β-anilinomethylene-cyanoacetate was prepared by the method of Snyder and Jones (*J. Amer. Chem. Soc.*, 1946, **68**, 1253). Ethyl β-anilino- and β-*m*-nitroanilinomethylene-acetoacetates were prepared by heating together equimolecular quantities of ethyl ethoxymethylene-acetoacetate and aniline or *m*-nitroaniline in a steam-bath. Ethyl β-arylaminomethylene-malonates were prepared by the method of Duffin and Kendall (*J. Chem. Soc.*, 1948, 893).

General Method of Bromination.—Bromine in chloroform or glacial acetic acid was slowly added to the ester solution in the same solvent. The reaction mixture was

allowed to stand at room temperature for the required period after which the separated product was filtered out, washed with a small amount of the solvent and dried. The yields registered varied from 30 to 34%. This product was then treated with water and in all such cases the liberated bromine from the side chain was estimated by Volhard's method.

Such a derivative of ethyl β-anilinomethylene-malonate, being highly unstable, lost the side-chain bromine so rapidly on isolation that it could not be investigated.

Bromination of ethyl β-anilinomethylene-acetoacetate formed ethyl αβ-dibromo-β-*op*-dibromoanilino product, which was filtered off. The filtrate, when diluted with water, furnished a mixture of ethyl β-*p*-bromo- and ethyl β-*op*-dibromo-anilinomethylene-acetoacetates, which were separated by fractional crystallisation from alcohol.

The products were confirmed, wherever possible, by their mixed melting points with authentic specimens obtained by the condensation of the corresponding bromo-amines and the esters. These products along with experimental conditions are described in Tables I and II.

TABLE I

Bromine taken.	Reaction time.	Bromo compounds.	M.P.	* Bromine. Total.	Side-chain.
		(1). Ethyl β-anilinomethylene-cyanoacetate (0.015 *M*) in $CHCl_3$ or acetic acid (100 c.c.).			
0.015*M*	3 days	Ethyl β-*p*-bromoanilinomethylene-cyanoacetate	151°	...	...
0.03*M*	Overnight	Ethyl αβ-dibromo-β-*p*-bromoanilinomethylene-cyanoacetate $C_{12}H_{11}O_2N_2Br_3$	116°-18° (decomp.)	53% (52.74%)	35.27% (35.16%)
		(2). Ethyl β-anilinomethylene-cyanoacetate (0.0185*M*) in $CHCl_3$ (25c.c.) or AcOH (35c.c.).			
0.074*M*	Do	Ethyl αβ-dibromo-β-*op*-dibromoanilinomethylene-cyanoacetate $C_{12}H_{10}O_2N_2Br_4$	106°-109° with decomp.	60.02(59.92)	30.00(29.96)
		(3). Ethyl β-anilinomethylene-acetoacetate and-malonate (0.015*M*) in $CHCl_3$ (100 c.c.).			
0.015*M*	Do	*p*-Bromoaniline hydrobromide	206° (decomp.)		...
0.060*M*	4 hours	*sym.*-Tribromoaniline hydrobromide	195° (decomp.)		...
		(4). Ethyl β-anilinomethylene-acetoacetate (0.01*M*) in acetic acid (100 c.c.).			
0.01*M*	1 hour	Ethyl-αβ-dibromo-β-*op*-dibromoanilinomethylene-acetoacetate $C_{13}H_{13}O_3NBr_4$	94°-96° (decomp.)	58.38(58.07)	29.06(29.038)
		(5). Ethyl β-anilinomethylene-malonate (0.015*M*) in acetic acid (100 c.c.).			
0.015*M*	½ hour	Ethyl β-*p*-bromoanilinomethylene-malonate	103°		...
0.03*M*	2 hours	Ethyl β-*op*-dibromoanilinomethylene-malonate $C_{14}H_{15}O_4NBr_2$	126°	37.85 (38.00)	
		(6). Ethyl β-*m*-nitroanilinomethylene-acetoacetate (0.015*M*) in acetic acid (100 c.c.).			
0.045*M*	Overnight	Ethyl αβ-dibromo-β-3-nitro-(?)-bromoanilinomethylene-acetoacetate $C_{13}H_{13}O_5N_2Br_3$	97°-101° (decomp.)	46.00(46.42)	30.54(30.94)
		(7). Ethyl β-*m*-nitroanilinomethylene-malonate (0.02*M*) in acetic acid (100 c.c.).			
0.06*M*	2 hours	3-Nitro-6-bromoaniline hydrobromide.	244° (decomp.).		...

* The figures in parenthesis refer to calculated values.

TABLE II

Treatment with water.

Parent substance.	Resulting product & formula.	M.P.	% Bromine. Found.	Calc.
1. Ethyl $\alpha\beta$-dibromo-β-*p*-bromoanilinomethylene-cyanoacetate	Ethyl-β-*p*-bromoanilinomethylene-cyanoacetate	151°	...	...
2. Ethyl $\alpha\beta$-dibromo-β-*op*-dibromoanilinomethylene-cyanoacetate	Ethyl β-*op*-dibromoanilinomethylene-cyanoacetate $C_{12}H_{10}O_2N_2Br_2$	199° (decomp.)	42.3	42.78
3. Ethyl $\alpha\beta$-dibromo-β-*op*-dibromoanilinomethylene-acetoacetate	Ethyl β-*op*-dibromoanilino-methylene-acetoacetate $C_{13}H_{13}O_3NBr_2$	160°	40.70	40.92
4. Ethyl $\alpha\beta$-dibromo-β-3-nitro-(?)-bromoanilinomethylene-acetoacetate	Ethyl β-3-nitro-(?)-bromoanilino-methylene-acetoacetate $C_{13}H_{13}O_5N_2Br$	143°	22.48	22.40

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CHEMISTRY DEPARTMENT,
M. T. B. COLLEGE,
SURAT.

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SYNTHESIS IN ACRIDINE SERIES. PART V. SYNTHESIS OF 5-METHYLACRIDINE DERIVATIVES

By Miss M. J. Sacha and S. R. Patel *

2:4-Dichloro-5-nitroacetophenone on being condensed with various aromatic amines has afforded the corresponding 2-acetyldiphenylamine derivatives in good yields. These have been cyclised to the corresponding 5-methylacridine derivatives. Similarly, 2:4-dichloroacetophenone has been condensed with aniline under the conditions of Ullmann's reaction and 2-acetyl-5-chlorodiphenylamine obtained has been cyclised to 2-chloro-5-methylacridine.

Although a considerable amount of work has been done on the synthesis of 5-N-substituted acridine derivatives related to atebrin, comparatively very little work has been done on the synthesis of 5-methylacridine derivatives. The present communication deals with the synthesis of 5-methylacridine derivatives containing substituents like NO_2, Cl and $-OMe$.

It is well known that a 5-chloroacridine derivative condenses with various amino compounds giving rise to the corresponding 5-N-substituted acridines due to the reactivity of the chlorine atom in this position (Magidson and Grigorowsky, *Ber.*, 1936, **69**, 396). Similarly 5-methylacridine, due to reactivity of the methyl group in this position, undergoes condensation with various reagents, giving rise to acridine derivatives with varied substituents in 5-position. As reported by Jensen and Homberger (*J. Amer. Chem. Soc.*, 1926, **48**, 800), 5-methylacridine condenses with formaldehyde, affording 5-(β-hydroxyethyl)-acridine ; the latter on oxidation yields acridine-5-carboxylic acid. Friedländer (*Ber.*, 1905, **38**, 2840) has shown that 5-methylacridine condenses with aromatic aldehydes, particularly nitrobenzaldehyde, to yield a 5-styrylacridine derivative. Kaufmann (*Ber.*, 1912, **45**, 1736) has reported that 5-methylacridine on condensation with *p*-nitrosodimethylaniline furnishes an anil which on subsequent hydrolysis gives rise to acridine-5-aldehyde. The hydrazone of the latter has been obtained on condensation of 5-methylacridine with diazotised aniline (Koshits and Kharkharov, *Chem. Abs.*, 1945, **39**, 1631).

Of the various methods available for the synthesis of 5-methylacridine, the simplest is that developed by Jensen and Rethwisch (*J. Amer. Chem. Soc.*, 1928, **50**, 1144). This method consists in two steps: (*i*) synthesis of 2-acetyldiphenylamine derivative containing the required substituents and (*ii*) its cyclisation to the corresponding 5-methylacridine derivative. This method has been used for the synthesis of 5-methylacridine derivatives described herein.

2-Acetyldiphenylamine is obtained by Ullmann's condensation of an *o*-aminoacetophenone derivative with halogeno-benzene or an *o*-halogeno-acetophenone with an aromatic amine (Perrina and Sargent, *J. Org. Chem.*, 1949, **14**, 583 ; Jensen and Rethwisch, *loc. cit.*). The former method though proceeds smoothly affording 2-acetyldiphenylamine derivative in good yield yet it has limited application as an *o*-aminoacetophenone,

* Present address: Dharmendra College, Rajkot.

simple or substituted, and is difficultly available ; hence the latter route consisting of the condensation of *o*-halogeno-acetophenone with an aromatic amine has been chosen for the synthesis of the required 2-acetyldiphenylamine derivatives.

Meyer (*Ber.*, 1922, **55**, 2054) has shown that the chlorine atom, *ortho* to the acetyl group in *o*-chloroacetophenone, is not labile enough to react with an aromatic amine. But Jensen and Rethwisch (*loc. cit.*) have shown that 2-chloro-5-nitroacetophenone condenses with various aromatic amines, giving rise to the corresponding 2-acetyldiphenylamine derivatives in excellent yield ; the obvious reason for this is the increased reactivity of the chlorine atom (*ortho* to the acetyl group) due to the presence of the nitro group in its *para* position.

It has been observed here that chlorine, *ortho* to the acetyl group, is also much less reactive even in 2 : 4- and 2 : 5-dichloroacetophenones. 2 : 4-Dichloroacetophenone condensed with aniline yielding 5-chloro-2-acetyldiphenylamine in extremely poor yield, while the condensation of 2 : 5-isomer with aniline failed. However, as expected, 2 : 4-dichloro-5-nitroacetophenone (I), obtained on nitration of 2 : 4-dichloroacetophenone, condensed with aromatic amines like aniline, *p*-chloroaniline, *p*-anisidine and α-naphthylamine, affording the corresponding 2-acetyldiphenylamine derivative in very good yield, the condensation of (I) with the aromatic amine having been brought about by heating the reactants in equimolecular proportions in presence of fused potassium acetate and using amyl alcohol as solvent. Use of potassium carbonate in place of the acetate and heating (I) with excess of aniline (or any aromatic amine) in presence of potassium acetate or carbonate did not prove suitable as the product obtained was highly coloured and appeared to be a mixture melting over a wide range of temperature.

The second step involving cyclisation of a 2-acetyldiphenylamine to the corresponding 5-methylacridine was effected by heating it with a solution of concentrated sulphuric acid in glacial acetic acid ; the use of concentrated sulphuric acid alone did not prove suitable due to the possibility of suphonation of the product of the reaction. The 2-acetyldiphenylamine derivatives, obtained from (I) and various aromatic amines, were cyclised by this method and the corresponding 5-methylacridine derivatives obtained, except 7-nitro-8-chloro-5-methyl-1 : 2-benzacridine, were purified by extracting them with boiling solution of hydrochloric acid (10%) and reprecipitating by ammonia, since they could not be satisfactorily purified by crystallisation. Sharp *et al.* (*J. Chem. Soc.*, 1943, 345) and Perrina and Sargent (*loc. cit.*) have reported that 5-methylacridines obtained on cyclisation of the required 2-acetyldiphenylamine derivative could not be satisfactorily crystallised from the usual solvents ; they have purified their products either by the above method or by subliming the product under reduced pressure. It would be interesting to note that these 5-methylacridine derivatives carrying a nitro group did not show any fluorescence in their solutions in acid or solvents like alcohol, acetone, etc.

The 2-acetyl-5-chlorodiphenylamine, obtained as a thick highly coloured semi-solid in a very low yield on Ullmann's condensation of 2 : 4-dichloroacetophenone with aniline, could not be isolated separately and the crude product was cyclised to obtain 2-chloro-5-methylacridine. It showed an intense green fluorescence in alcohol and acid solutions.

Further work on the study of the condensation reactions of these 5-methylacridine derivatives with various reagents, mentioned before, is in progress.

EXPERIMENTAL

2 : 4-Dichloro- and 2 : 5-dichloro-acetophenones were obtained by Friedel-Crafts' acetylation of *m*- and *p*-dichlorobenzene respectively, following the method described by Shodhan, Kshatriya and Nargund (this *Journal*, 1947, **24**, 373).

2-Chloro-5-methylacridine.—2 : 4-Dichloroacetophenone (3 g.), fused potassium carbonate (3 g.), freshly distilled aniline (10 c.c.), a trace of Cu powder and a little cuprous iodide were refluxed at 180-85° for 3 hours. The reaction mixture was steam-distilled, cooled and extracted with ether. The dark coloured liquid which remained behind on removal of ether was extracted with glacial acetic acid (15 c. c.) containing H_2SO_4 (conc., 3 c. c.), and the solution was heated on a water-bath for 2 hours. The resulting solution showing an intense green fluorescence was made alkaline and the yellowish product separating was dissolved in boiling HCl solution (10%). The acid extract was cooled and made alkaline when 2-chloro-5-methylacridine separated out as a yellowish light powder. It crystallised from petrol-ether in small yellow needles, m.p. 105-106°, yield 0.10 g. It showed an intense green fluorescence in alcohol and in acid solutions. (Found : Cl, 15.8. $C_{14}H_{10}NCl$ requires Cl, 15.6%).

The condensation of 2 : 5-dichloroacetophenone with aniline under the conditions of Ullmann's reaction did not succeed.

2 : 4-Dichloro-5-nitroacetophenone.—2 : 4-Dichloroacetophenone (10 g.) was added in small lots to fuming nitric acid (50 c. c., *d* 1.5), cooled in an ice-bath at such a rate as not to allow the temperature to rise above 5°. The reaction mixture was left in an ice bath for about 2 hours and decomposed by pouring it over crushed ice. The product separating was collected and washed with a large excess of water. It crystallised from alcohol in yellow stout needles, m.p. 62°, yield 10 g. (Found : Cl, 30.7. $C_8H_5O_3NCl_2$ requires Cl, 30.4%).

The *oxime* of the above ketone crystallised from dilute alcohol in yellowish needles, m.p. 128°. (Found : Cl, 28.7. $C_8H_6O_3N_2Cl_2$ requires Cl, 28.5%).

2 : 4-Dichloro-5-nitrobenzoic Acid.—A mixture of 2 : 4-dichloro-5-nitroacetophenone (2 g.) and $KMnO_4$ solution (150 c. c., 3%) was heated on a water-bath with constant stirring till the permanganate colour disappeared. The resulting manganese dioxide was filtered and the filtrate evaporated to half its bulk and acidified. The product separating was collected and crystallised from boiling water in yellowish small needles, m. p. 160°. (Found : Equiv., 232 ; Cl, 30.5. $C_7H_3O_4NCl_2$ requires equiv., 236 ; Cl, 30.1%).

2-Acetyl-4-nitro-5-chlorodiphenylamine.—The conditions described below for this condensation were established after studying it under various experimental conditions.

2 : 4-Dichloro-5-nitroacetophenone (10 g.), freshly distilled aniline (10 c. c.), fused potassium acetate (5 g.) and *iso*amyl alcohol (50 c. c.) were refluxed at 125-30° for 2 hours. The reaction mixture was then steam-distilled to remove amyl alcohol and the residual thick liquid, sticking to the sides of the reaction flask, was washed with water and dissolved in minimum quantity of boiling alcohol and filtered. From this solution, on keeping, the product crystallised out as a heavy yellow powder, m. p. 104°, yield 13 g. (Found : Cl, 12.4. $C_{14}H_{11}O_3N_2Cl$ requires Cl, 12.2%).

2-Chloro-3-nitro-5-methylacridine.—A solution of the preceding amine (5 g.) in glacial acetic acid (50 c.c.) containing H_2SO_4 (conc., 2.5 c.c.) was refluxed at 130°

for 2 hours. The reaction mixture was then decomposed by pouring it over crushed ice and made just alkaline. The brown product separating was collected and extracted with boiling HCl solution ; a large portion of the product remained unextracted in the form of a dark sticky solid. The cooled acid extract was made alkaline when 2-chloro-3-nitro-5-methylacridine separated out as a brownish yellow powder. It was filtered, washed and dried in air. It could not be satisfactorily crystallised from usual solvents. It did not melt up to 300°, yield 2 g. (Found : Cl, 13.2. $C_{14}H_9O_2N_2Cl$ requires Cl, 13.0%).

4-Nitro-5-chloro-4′-methoxy-2-acetyldiphenylamine was obtained, as described above, by refluxing a mixture of 2 : 4-dichloro-5-nitroacetophenone (10 g.), *p*-anisidine (10 g.), fused potassium acetate (5 g.) and *iso*amyl alcohol (50 c.c.). It crystallised from alcohol in fine yellow granules, m. p. 124°, yield 14 g. (Found : Cl, 11.35. $C_{15}H_{13}O_4N_2Cl$ requires Cl, 11.10%).

2-Chloro-3-nitro-7-methoxy-5-methylacridine, obtained on cyclisation of the above mentioned 2-acetyldiphenylamine derivative following the method described above, was purified by extraction with boiling HCl solution (10%) and reprecipitating it with alkali in light brown powder. It darkened at 195° and did not melt up to 300°. (Found: Cl, 11.97. $C_{15}H_{11}O_3N_2Cl$ requires Cl, 11.70%).

4-Nitro-5 : 4′-dichloro-2-acetyldiphenylamine was obtained, as above, by condensing 2 : 4-dichloro-5-nitroacetophenone with *p*-chloroaniline. It crystallised from alcohol in bright yellow powder, m. p. 152°. (Found : Cl, 22.1. $C_{14}H_{10}O_3N_2Cl_2$ requires Cl, 21.8%).

2 : 7-Dichloro-3-nitro-5-methylacridine was obtained on cyclisation of the above mentioned diphenylamine derivative, following the procedure described above. It was purified by extracting it with boiling dilute HCl solution. It crystallised from benzene-petrol mixture in brown powder. It did not melt up to 300°. (Found : Cl, 23.4. $C_{14}H_8O_2N_2Cl_2$ requires Cl, 23.1%).

Condensation of 2 : 4-Dichloro-5-nitroacetophenone with α-Naphthylamine : Formation of 3-Nitro-4-chloro-6-(α-naphthyl)-aminoacetophenone.—2 : 4-Dichloro-5-nitroacetophenone (5 g.), α-naphthylamine (5 g.), fused potassium acetate (2.5 g.) and *iso*amyl alcohol (25 c.c.) were refluxed at 130° for 2 hours. The yellow product left on removal of *iso*amyl alcohol by steam-distillation was collected and crystallised from alcohol in yellow granules, m. p. 201-202°, yield 5 g. (Found : Cl, 10.56. $C_{18}H_{13}O_3N_2Cl$ requires Cl, 10.40%).

7-Nitro-8-chloro-5-methyl-1 : 2-benzacridine.—The above mentioned diphenylamine derivative (3 g.) was dissolved in glacial acetic acid (30 c. c.) containing H_2SO_4 (conc., 3 c.c.) and the solution was heated on a water-bath for an hour. The reaction mixture was then poured in ice and made just alkaline with ammonia. The yellow solid which separated out was collected and dried. It crystallised from benzene-petrol mixture in light brown powder, m. p. 242-44° (decomp.). (Found: Cl, 11.2. $C_{18}H_{11}O_2N_2Cl$ requires Cl, 11.0%).

M. R. Science Institute,
Gujarat College,
Ahmedabad.

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ACTION OF ALKALINE IODINE SOLUTION ON ACETALDEHYDE

By Sameer Bose

There are two competing reactions taking place, one is iodine substitution resulting in the formation of iodoform and another is oxidation of the aldehyde to acetic acid. Iodoform has been estimated and the presence of acetate ions detected by the lanthanum nitrate method. On diluting the reaction mixture with plenty of water and increasing the alkali concentration, it is possible at low temperatures to convert 98% of the aldehyde to iodoform, whereas under suitable conditions 99% of the aldehyde can be oxidised to acetic acid. There is indication to show that OI^- ions are responsible for iodine substitution and the unionised HOI molecules act as oxidant.

In a quantitative study of this reaction, Hitcher and Mueller (*Trans. Roy. Soc. Canada*, 1929, **3-23**, III, 35) reported that under the most favourable conditions it was carried only to 60% of completion. They estimated the amount of iodine consumed and inferred that only iodoform reaction had occurred. Dal Nogare *et al.* (*Anal. Chem.*, 1951, **23**, 1473) who extracted the iodoform produced with chloroform and estimated it by finding its absorbtion at 347 mμ came to a similar conclusion. Mitchell *et al.* ("Organic Analysis", 1953, Vol. I, p. 268) compared the extents of the reaction by various compounds which produced iodoform with alkaline iodine solution and concluded that in case of acetaldehyde the reaction was not stoichiometrically complete and the conversion to iodoform was the lowest. The present work was undertaken with a view to ascertaining the cause of the low results. It deals specially with the effect of dilution, temperature, alkali concentration and excess of iodine on the course of the reaction which has been studied by determining the amount of iodine consumed and the iodoform produced.

Experimental

A stock solution of 0.05 *M* acetaldehyde was prepared by dissolving a pure sample of the aldehyde in water and standardising it with hydroxylamine sulphate. The procedure followed was that described by Kolthoff and Stenger ("Volumetric Analysis", 1947, Vol. II, p. 224).

Effect of Dilution and Temperature.—Solutions of 0.005*M* acetaldehyde (5 c.c.) and 0.02*N*-I_2 (10 c.c.) were treated with varying quantities of water and then made to react by adding quickly 4*N*-NaOH solution (5c.c.) with vigorous swirling of the reacting solutions. Three sets of experiments were carried out at 3 different temperatures, viz., to 5°, 20° and 35°. The time allowed for completion of the reaction was 4 to 5 hours at 5°, 1 hour at 20° and ½ hour at 35°. On completion of the reaction, the mixture was acidified with 4*N*-H_2SO_4 (5.5 c.c.) and the iodine liberated was titrated with 0.02*N* hypo solution taken in a 10 c.c. microburette. A blank was carried out similar in all respects except for the addition of acetaldehyde solution, instead of which 200 c.c. of water was used.

With increase in dilution of the reacting solutions, the amount of I_2 consumed was found to increase. Theoretically if all the CH_3CHO were converted to in CHI_3, each molecule of the aldehyde would consume 6 atoms of I_2.

$$CH_3CHO + 3I_2 + 4NaOH \rightarrow CHI_3 + HCOONa + 3NaI + 3H_2O.$$

At ordinary dilution 3.6 atoms of iodine are consumed per molecule of the aldehyde and this corresponds to 60% reaction reported by previous workers. However, in very dilute solutions it is possible at 5° to convert 98% of the aldehyde in to CHI_3, as illustrated in Table I.

TABLE I

[0.005*M*-Acetaldehyde (5 c.c.) + 0.02*N*-I_2 (10 c.c.) + H_2O + 4*N*-NaOH (5 c.c.).].

Expt. No.	Water added.	Molality of CH_3CHO in the reaction mixture.	Iodine (g. atom) consumed per molecule of acetaldehyde at		
			5°.	20°.	35°.
1	0 c.c.	12.50×10^{-4}	3.81	3.60	3.51
2	50	3.57	5.00	4.80	4.65
3	100	2.10	5.51	5.40	5.20
4	150	1.47	5.75	5.62	5.43
5	200	1.14	5.88	5.78	5.52
6	250	0.92	5.90	5.75	5.58
7	300	0.78	5.90	5.75	5.60
8	400	0.60	5.90	5.76	5.60

Effect of Alkali Concentration.—The amount of CHI_3 produced was found first to increase with the increase in alkali concentration, but it soon reached a maximum value and with further increase in alkali, the value gradually decreased. The optimum concentration of the alkali, affording the maximum yield of CHI_3, varied with the concentrations of the CH_3CHO and I_2 solutions. In a series of experiments the same volume of very dilute solution of CH_3CHO and I_2 was treated with 4*N*-NaOH, varying from 0.1 c.c. to 10 c.c. The amount of I_2 consumed was plotted against the alkali concentration, taken as base. The curve showed a steep rise in the beginning and soon attained a peak, which was flat due to the I_2 consumption remaining the same for a considerable change in the alkali concentration, and later it showed a gradual downward trend.

Effect of Excess of Iodine.—A large excess of iodine was found to afford a lower % conversion of CH_3CHO to CHI_3, as judged from the amount of I_2 consumed. Table II illustrates the results of experiments carried out at 20° with concentration of all the reactants, except that of I_2, being kept the same. The alkali added was sufficient to convert all the I_2 into NaOI.

TABLE II

[0.005*M*-CH_3CHO (5 c.c.) + 200 c.c. water + 0.02*N*-I_2 soln. + 4*N*-NaOH (10 c.c.)].

Expt. No.	I_2 added in excess.	0.02 *N*-I_2 consumed.	Expt. No.	I_2 added in excess.	0.02 *N*-I_2 consumed.
1	10%	7.3 c.c.	4	75%	7.1 c.c.
2	25	7.3	5	100	7.1
3	50	7.2	6	200	6.9
			Theoretical value (iodoform reaction)		7.5

Iodoform Estimated.—The amount of CHI_3 produced in these reactions was very small and could not be accurately estimated by ordinary methods. A new procedure has been developed the details of which are under publication. The method consists in exposing a solution of CHI_3 in ether-benzene mixture along with 0.01*N* hypo solution to sunlight for 30-40 minutes with occasional shaking, when the CHI_3 decomposes quantitatively to free I_2, which is estimated by titrating the excess of the hypo solution. Synthetic mixtures of CHI_3 and water were estmated by this method and the error did not exceed 1.0%. In Table III the experimental and the calculated values of CHI_3, obtained from CH_3CHO, are compared. The calculated values have been arrived at by using the formula mentioned in the Discussion.

TABLE III

[0.025*M*-CH_3CHO (5 c.c.) + water added + 0.05*N*-I_2 (20 c.c.) + 4*N*-NaOH (4 c.c.)].

Expt. No.	Water added.	0.05 *N*-I_2 consumed.	Iodoform. Found.	Calc.
1	Nil	9.1 c.c.	19.7 mg.	20.2 mg.
2	50 c.c.	11.5	31.5	32.0
3	100	12.7	38.1	38.0
4	150	13.1	39.4	39.9
5	200	13.4	40.1	41.4
6	300	13.9	42.8	43.8

Prevention of Iodoform Formation.—The CHI_3 reaction could be suppressed to a large extent by using about 10% less alkali than the amount required theoretically. To the mixture of acetaldehyde and iodine 1*N*-NaOH solution was added slowly dropwise from a burette, while the reacting solutions were vigorously shaken with a circular motion. The reactions were carried out at 25-30° and the time allowed for completion was 20 minutes. Later the excess of I_2 was estimated by acidifying the solution with H_2SO_4 and titrating with 0.05*N* hypo. There was no visible precipitate of CHI_3, but the clear solution possessed a faint smell of it. The minute quantity present was later estimated by photochemical decomposition in sunlight. Assuming that only oxidation of the CH_3CHO molecule takes place, then 2 atoms of iodine will be consumed per molecule of the aldehyde

$$I_2 + 3NaOH + CH_3CHO \rightarrow CH_3COONa + 2\,NaI + 2\,H_2O.$$

The experimental and the calculated values of I_2 consumed, recorded in Table IV, compare favourably. Based on these observations, a procedure has been devised for estimating acetaldehyde by oxidising it quantitatively (this *Journal*, 1957, **34**, 739). The presence of acetate ions was detected in the reaction products. After the reaction was over the mixture was treated with excess of alkali and evaporated to dryness for concentrating the acetate ions. The solid residue was treated with a small amount of HCl (conc.) and warmed after adding a few drops of lanthanum nitrate and ammonium hydroxide solutions. I_2 was already present in the solution. A good blue precipitate as described by Vogel ("Qualitative Chemical Analysis", 1948, p. 307) was obtained. The blue colour is said to be due to the adsorption of I_2 on the basic acetate of lanthanum.

TABLE IV

CH_3CHO soln. taken (0.05 *M*).	0.1*N*-I_2 added.	NaOH added (1.0*N*).	0.1*N*-I_2 consumed. Found.	Calc.	CHI_3 estimated.	CH_3CHO converted to CHI_3.
2 c.c.	10 c.c.	0.9 c.c.	2.05 c.c.	2.0 c.c.	0.4 mg.	1.0%
5	20	1.8	5.05	5.0	0.4	0.4
7.5	30	2.7	7.60	7.5	0.8	0.6
10	40	3.6	10.20	10.0	1.3	0.7
15	75	6.7	15.20	15.0	1.9	0.7
20	100	9.0	20.30	20.0	2.6	0.7

DISCUSSION

It is evident from the data presented above that there are two reactions taking place, one is oxidation of the aldehyde to acetic acid and another is the substitution of I_2 in the aldehyde molecule. The intermediate compound, CI_3CHO, is probably unstable and decomposes readily in presence of alkali to CHI_3. Woo and Chu (*Science Record*, 1949, **2**, 280) have also stated that the iodoform reaction of CH_3CHO is probably accompanied by oxidation of the molecule.

If the quantity of CH_3CHO is known and the amount of I_2 consumed is determined, then it is possible to calculate the amounts of CHI_3 and acetic acid produced. In the iodoform reaction every molecule of the aldehyde consumes six atoms of iodine whereas in the oxidation reaction, two atoms are consumed. So if x is the fraction of an acetaldehyde molecule undergoing I_2 substitution, then

$$6x + 2(1-x) = \text{number of I atoms consumed per molecule of } CH_3CHO.$$

Using this formula the amount of CHI_3 produced has been calculated and compared with the experimental values (Table III). The fair agreement between the two shows that the present contention of two simultaneous reactions is correct.

Probable Mechanism of the Reaction.—The reaction of iodine with CH_3CHO to furnish iodoform is probably brought about by OI^- ions, and the oxidation of the aldehyde to acetic acid by the unionised molecules of HOI. The following points are adduced in support of this view.

(1) As NaOI is the salt of a very weak acid, it hydrolyses profusely to HOI and NaOH (Ephraim, "Inorganic Chemistry", 1939, p. 361). Hence, in a mixture of I_2 and NaOH, where I_2 is in excess, the concentration of OI^- ions will be very small and therefore such a mixture oxidises 99.3% of the aldehyde, as illustrated in Table IV. Moreover, the presence of OI^- ions cannot be completely eliminated and so the formation of CHI_3 cannot be avoided altogether.

(2) Excess of alkali affects the reaction in various ways. Its actions are summarised below:

$$(i)\quad I_2 + 2Na^+OH^- \rightleftharpoons Na^+OI^- + Na^+I^- + H_2O$$

$$(ii)\quad Na^+OI^- + H_2O \rightleftharpoons Na^+OH^- + HOI$$

$$(iii)\quad 3OI^- + CH_3CHO \rightleftharpoons CI_3CHO + 3OH$$

On increasing the alkali concentration, the equilibrium of the reaction (*i*) shifts to the right with the result that more of NaOI is produced. In the same reaction it has been found that even on adding twice the amount of alkali theoretically required, some free I_2 exists as indicated by starch solution, and only after adding ten times the theoretical quantity of alkali all the I_2 is converted in to NaOI. But the velocity of iodination continues to increase with alkali concentration even at this stage when no more of free I_2 exists. This is because OI^- ions, which are responsible for iodination, continue to increase due to the reversal of the reaction (*ii*) being promoted by the excess of alkali. Lastly, alkali tends to retard the iodination process as indicated in reaction (*iii*). Therefore increase in alkali concentration first accelerates the rate of iodination and later retards it, as found experimentally.

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CHEMICAL LABORATORIES,
MAHAKOSHAL MAHAVIDYALAYA,
JABALPUR.

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SEARCH FOR NEW INSECTICIDES. PART I

By S. S. Tiwari and A. Singh

o-Hydroxyketones of five esters of 2-bromo-4-*tert.*-butylphenol have been prepared by the Fries rearrangement and converted into their allyl ethers with a view to studying their insecticidal activity.

A good contact insecticide must have a combination of a toxic and a lipoid-soluble groupings in its molecule (Lauger *et al.*, *Helv. Chim. Acta*, 1944, **27**, 918). The toxic groupings can be obtained by introducing the residues of inhalation narcotics into the insect poisonous components. Validity of this hypothesis was justified by Lauger *et al.* (*loc. cit.*), who showed that allyloxy-aryl ethers were good contact insecticides. Keeping this in view, we have prepared five compounds containing allyl groups as toxophores and the ether linkage having lipophilic properties (cf. Chen and Sumerford, *J. Amer. Chem. Soc.*, 1951, **73**, 4694). These compounds also contain a ketonic group which would increase the lipoid solubility and may further enhance their insecticidal activity.

Five esters of 2-bromo-4-*tert.*-butylphenol, viz., acetate, propionate butyrate, caproate and heptoate, were obtained by the action of the appropriate acid chloride on the phenol. The Fries rearrangement of these esters was studied at 110° without a solvent.

In all the cases studied, *o*-hydroxyketones were obtained, exhibiting red coloration with 1% ferric chloride solution, and forming yellow crystalline solids with dilute 2% caustic soda solution (cf. Pyman, *J. Chem. Soc.*, 1930, 280).

Experimental

The esters of 2-bromo-4-*tert.*-butylphenol, prepared by the method of Spasov, described earlier (Sen and Tiwari, this *Journal*, 1932, **29**, 358), are summarised in Table I.

Table I

2-Bromo-4-*tert.*-butylphenyl esters.	Yield	B. P.	Mol. formula	% Carbon. Found.	% Carbon. Calc.	% Hydrogen. Found.	% Hydrogen. Calc.
Acetate	97%	120°/8 mm	$C_{12}H_{15}O_2Br$	52·92	53·14	5·52	5·54
Propionate	93	128°/3	$C_{13}H_{17}O_2Br$	54·46	54·74	5·93	5·97
Butyrate	80	148°/2	$C_{14}H_{19}O_2Br$	55·95	56·18	6·32	6·35
Caproate	96	145°/2	$C_{16}H_{23}O_2Br$	59·11	59·34	6·91	6·93
Heptoate	98	148°/2	$C_{17}H_{25}O_4Br$	59·61	59·81	7·30	7·33

The Fries Rearrangement of the Esters: Rearrangement at 110°.—The ester (0.1*M*) was rearranged by keeping it with anhydrous aluminium chloride (0.15*M*) at 110° for 2 hours. The hydroxyketones were isolated, purified and characterised in the usual way (Table II). The method has been described by Sen and Tiwari (*loc. cit.*). The *o*-hydroxyketones obtained by the Fries rearrangement of these esters were converted into their allyl ethers. These were characterised through their 2:4-dinitrophenylhydrazones. The work on the insecticidal activity of these compounds is in progress.

TABLE II

Bromo-4-*tert.*-butyl-phenyl esters.	Ketone formed.	Yield.	B.P.	Ketones % Carbon. Found.	Ketones % Carbon. Calc.	Ketones % Hydrogen Found	Ketones % Hydrogen Calc.	2:4-Dinitrophenylhydrazones. M.P.	Mol. Formula.	% Nitrogen. Found.	% Nitrogen. Calc.
Acetate	R-methyl-K	54%	142°/3 mm	52.92	53.14	5.51	5.54	200°	$C_{18}H_{19}O_5N_4Br$	12.39	12.41
Propionate	R-ethyl-K	68	165°/3	54.51	54.74	5.94	5.96	225°	$C_{19}H_{21}O_5N_4Br$	11.91	12.04
Butyrate	R-*n*-propyl-K	65	150°/2	55.94	56.18	6.34	6.35	175°	$C_{20}H_{23}O_5N_4Br$	11.39	11.69
Caproate	R-*n*-amyl-K	68	210°/9	59.03	59.34	6.93	6.93	136°	$C_{22}H_{27}O_5N_4Br$	11.03	11.05
Heptoate	R-*n*-hexyl-K	65	200°/2	59.43	59.81	7.30	7.33	140-41°	$C_{23}H_{29}O_5N_4Br$	10.59	10.75

K = ketone ; R = 2-hydroxy-3-bromo-5-*tert.*-butlyphenyl.

N.B. The molecular formula of the ketone is the same as of the ester.

TABLE III

Hydroxy-ketone.	Ether formed.	Yield.	B.P.	Mol. formula.	Ethers % Carbon. Found	Ethers % Carbon. Calc.	Ethers % Hydrogen. Found.	Ethers % Hydrogen. Calc.	2:4-Dinitrophenylhydrazones. Mol. formula.	M.P.	%Nitrogen. Found.	%Nitrogen. Calc.
R-methyl-K	R'-methyl-K	66%	115°/1 mm	$C_{15}H_{19}O_2Br$	57.65	57.88	6.10	6.11	$C_{21}H_{23}O_5N_4Br$	165°	11.30	11.53
R-ethyl-K	R'-ethyl-K	65	135°/1	$C_{16}H_{21}O_2Br$	59.01	59.07	6.43	6.46	$C_{22}H_{25}O_5N_4Br$	157°	10.64	11.09
R-*n*-propyl-K	R'-*n*-propyl-K	56	195°/16	$C_{17}H_{23}O_2Br$	59.97	60.17	6.77	6.78	$C_{23}H_{27}O_5N_4Br$	130°	10.45	10.79
R-*n*-amyl-K	R'-*n*-amyl-K	76	165°/1	$C_{19}H_{27}O_2Br$	61.95	62.11	7.20	7.39	$C_{25}H_{31}O_5N_4Br$	129°	10.11	10.26
R-*n*-hexyl-K	R'-*n*-heptyl	68	164°/1	$C_{20}H_{29}O_2Br$	64.09	64.30	7.33	7.34	...	...	...	...

K = ketone.

R = 2-Hydroxy-3-bromo-5-*tert.*-butylphenyl.

R' = 2-Allyloxy-3-bromo-5-*tert.*-butylphenyl.

N.B. 2-Allyloxy-3-bromo-5-*tert.*-butylphenyl-hydrazone has not formed.

Allyl-aryl Ethers.—A mixture of allyl bromide (0.11*M*), freshly fused potassium carbonate (0.15*M*) and 80 c.c. of anhydrous acetone was refluxed on a water-bath for 8 hours. A heavy precipitate of potassium halide began to form soon after the refluxing was started. After cooling, ice was added and the acetone was distilled off. The oily layer was extracted with ether. The ether layer was washed with 5% caustic soda solution several times, then with distilled water and dried over freshly fused potassium carbonate. The ether was then removed by distillation and the residual oil distilled under reduced pressure (Table III).

The authors wish to thank Dr. A. B. Sen for his kind interest in this work.

CHEMISTRY DEPARTMENT,
LUCKNOW UNIVERSITY, LUCKNOW.

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SYNTHESIS OF 8-AMINOQUINOLINES. PART VI*

By Achintya K. Sen and U. P. Basu

The preparation of 5-chloro- and 7-chloro-8-aminoquinaldines, which are necessary intermediates in the synthesis of antimalarials in the 8-aminoquinoline series, has been described.

The chloroquinaldines required for the present work were prepared by the method of Doebner and Miller (*Ber.*, 1881, **14**, 2816 ; 1883, **16**, 2404 ; 1884, **17**, 1659) as modified by Utermohlen (*J. Org. Chem.*, 1943, **8**, 544) and Bowen *et al.* (*J. Amer. Chem. Soc.*, 1953, **75**, 4307). Utermohlen (*loc. cit.*) has described a valuable modification of the Skraup and Doebner-Miller synthesis using *m*-nitrobenzenesulphonic acid as water-soluble acid oxidising agent. Applying the procedure with a slight further modification Spivey and Curd (*J. Chem. Soc.*, 1949, 2656) obtained a maximum yield of 60% of the usual mixed 5- and 7- isomers in the preparation of chloroquinaldines from *m*-chloroaniline. In the original procedure of Utermohlen equimolecular amounts of amine and aldehyde were employed and the yields varied between 40 and 60%. It has been recently shown by Bowen *et al.* (*loc. cit.*) that using the ratio of aldehyde to amine as 1.67 : 1, instead of equimolecular amounts, the yields rose as high as 80%. Following the above modifications the mixture of chloroquinaldines has been isolated in the present work in 80% yield.

The mixture was directly nitrated with potassium nitrate and 100% sulphuric acid, without separating the isomeric 5- and 7-chloroquinaldines. The less basic 7-chloro-8-nitroquinaldine separated out on pouring the reaction mixture from nitration operation into ice-water. The mother-liquor, after removing the 7-chloro-8-nitroquinaldine, was basified to yield the corrresponding 5-chloro derivative. The position of the nitro group in 7-chloro-8-nitroquinaldine was established by its reduction to known 8-aminoquinaldine by red phosphorus and hydriodic acid. The structure of 7-chloro-8-aminoquinaldine has been further confirmed by converting the aminoquinaldine to 7 : 8-dichloroquinaldine through the Gatterman reaction and comparing the product with an authentic sample of 7 : 8-dichloroquinaldine, prepared by the modified Doebner-Miller reaction upon 2 : 3-dichloroaniline. The structure of 5-chloro-8-nitroquinaldine was ascertained from its direct synthesis from 5-chloro-2-nitroaniline. The aminoquinaldines were obtained by reduction of the nitro compounds with iron and acetic acid, "Sulfo-mix" (a solution of *m*-nitrobenzenesulphonic acid in sulphuric acid), which was required in the present work, was prepared as described by Utermohlen (*loc. cit.*).

*The present work was completed in 1953 on a project under the auspices of the Council of Scientific and Industrial Research. The publication was delayed due to one of the authors' (A. K. S.) mission to U. S. A.

EXPERIMENTAL

5-& 7-Chloroquinaldines.—In an one-litre, 3-necked flask, equipped with a mercury-sealed stirrer, thermometer and a condenser provided with a dropping funnel at the top, were placed 100 c.c. of water and 404 g. of 'sulfo-mix'; *m*-chloroaniline (127.5 g.) was added to the mixture with stirring. The mixture was then heated in an oil-bath to 105° and crotonaldehyde (117 g.) was added with vigorous stirring over a period of 45 minutes while the mixture was held at 105-10° by intermittent heating and cooling. The temperature was then slowly raised to 125° during one hour. The foaming, when became excessive, was controlled by momentarily removing the oil-bath from time to time. The reaction mixture was then cooled, poured into about 1500 g. of ice and basified with a slight excess of caustic soda solution. The crude product was then distilled with steam and about 20 litres of distillate was collected. The oily layer was separated and the aqueous layer was once extracted with ether. The solvent was then removed from the dried ($CaCl_2$) extract and the residual oil was distilled at ordinary pressure to furnish a slightly yellow oily liquid in 80% yield; b.p. 275-82°.

7-Chloro-8-nitro and 5-Chloro-8-nitroquinaldines.—The above mixture of chloroquinaldines (35.7 g.) was dissolved in a mixture of 15 c.c. of fuming sulphuric acid (60% SO_3) and 100 c.c. of concentrated sulphuric acid. To the stirred and well-cooled mixture potassium nitrate (27 g.) was added during one hour while the temperature was maintained at 0° to -5°. After stirring at that temperature for 3 hours, the mixture was kept overnight at room temperature and poured into 500 g. of crushed ice, stirred well, filtered and the solid was washed thoroughly till free of acid. The crystalline product obtained was recrystallised from rectified spirit to afford 18 g. of pure 7-chloro-8-nitroquinaldine melting at 145-46°. (Found: N, 12.34. $C_{10}H_7O_2N_2Cl$ requires N, 12.58%).

The acid solution after removal of 7-chloro isomer was basified with a slight excess of caustic soda when a solid separated. This was collected, washed and crystallised from rectified spirit to yield 8 g. of 5-chloro-8-nitroquinaldine, m.p. 131-32°. (Found: N, 12.81. $C_{10}H_7O_2N_2Cl$ requires N, 12.58%).

Reduction of 7-Chloro-8-nitroquinaldine with Red Phosphorus and Hydriodic Acid to 8-Aminoquinaldine.—A mixture of 7-chloro-8-nitroquinaldine (5 g.), potassium iodide (6 g.), red phosphorus (4 g.) and constant boiling hydriodic acid (40 c.c.) was heated under reflux. After the initial vigorous reaction had subsided, a further quantity of hydriodic acid was added and the heating under reflux was continued for 5 hours. After the period was over, 10 c.c. of water was added to the mixture, heated to boiling and filtered hot. The cooled solution was then basified with a slight excess of caustic soda, filtered and the solid was washed thoroghly with water and crystallised from ligroin, m.p. 55-56°. The mixed m.p. with an authentic sample was 56°, prepared according to Doebner and Miller (*Ber.*, 1884, **17**, 1701), recorded no depression.

5-Chloro-8-nitroquinaldine from 5-Chloro-2-nitroaniline.—In a 100 c.c. bolt headed flask fitted with a short air-condenser, dropping funnel and a thermometer dipping below

the surface of the liquid were placed water (5 c.c.) 'sulfo mix' (20 g.) and 2-nitro-5-chloroacetanilide (7.2 g.). The solution was heated in an oil-bath at 130° for 30 minutes and the mixture was then cooled to 105° and crotonaldehyde (4 g.) was added with vigorous shaking (temperature was maintained at 105-110°) during 20 minutes. When the addition was over, the temperature was gradually raised to 125° and then to 130° and kept at that temperature for half an hour. The mixture was then poured into iced caustic soda solution, filtered, washed thoroughly with water, dried and extracted with ether. Ether was evaporated off and the residue was crystallised from rectified spirit, m.p. 128-30°. The mixed m. p. with a sample, prepared by the nitration procedure described earlier, recorded no depression.

7-Chloro-8-aminoquinaldine.—A mixture of 7-chloro-8-nitroquinaldine (13.3 g.) and 50% acetic acid (120 c.c.) was heated on a steam-bath. Powdered iron (80 mesh, 10 g.) was added in small portions over a period of 1½ hours to the vigorously stirred mixture. The heating was continued for one hour more after the last portion of iron added. The mixture was cooled, made alkaline with aqueous NaOH and the 7-chloro-8-aminoquinaldine was distilled with steam. The oily layer was separated from about 4 litres of the distillate which was collected, and the aqueous portion was extracted once with ether. After distilling off the ether from the dried extract, the residual oil was distilled under reduced pressure, yield 9.5 g., b.p. 170°/5 mm. (Found: N, 14.00. $C_{10}H_9N_2Cl$ requires N, 14.54%).

The *picrate* was prepared by adding an alcoholic solution of picric acid to a solution of 7-chloro-8-aminoquinaldine; the picrate which separated out immediately was collected and recrystallised from rectified spirit in shining yellow crystalline solid, m.p. 197-99°.

7-Chloro-8-acetamidoquinaldine.—7-Chloro-8-aminoquinaldine (0.5 g.) was acetylated by boiling in 5 c.c. of acetic anhydride for about 15 minutes and then poured in ice-water. The supernatant aqueous portion was decanted off and the semi-solid mass was treated with fresh water. The crystalline solid was collected, washed with water and recrystallised from aqueous alcohol, m.p. 142-44°. (Found: N, 11.45. $C_{12}H_{11}ON_2Cl$ requires N, 11.92%).

7:8-Dichloroquinaldine.—(*a*). A solution of sodium nitrite (3.2 g.) in water (10 c.c.) was added to a solution of 7-chloro-8-aminoquinaldine (8.5 g.) in aqueous HCl (80 c.c. in 60 c.c. water) at 0° to -5°. A suspension of copper-bronze (10 g.) in aqueous HCl (1 c.c. in 10 c.c. water) was added slowly to the solution of the diazotised amine. When no more gas evolved, the mixture was heated on a water-bath for half-an-hour, made strongly alkaline with ammonium hydroxide and was distilled with steam. The solid collected from the distillate was recrystallised from aqueous alcohol, m.p. 70-71°. (Found: N, 6.45. $C_{10}H_7NCl_2$ requires N, 6.60%). The m.p. remained undepressed on admixture with an authentic 7:8-dichloroquinaldine, prepared from 2:3-dichloroaniline as described in (*b*).

(*b*). In a wide pyrex test tube, fitted with a condenser and a thermometer dipping below the surface of the mixture, were placed 'sulfo mix' (22.5 g.) and water (5.5 c.c.). 2:3-Dichloroaniline (8.9 g.) was slowly added to the mixture with cooling. The tube

was then gradually heated to 105°, and 6.5 g. of crotonaldehyde was slowly added during 20 minutes with shaking, while the temperature was maintained at 105-10°. After the addition was over the temperature was slowly raised to 130°, kept at that temperature for 10 minutes, poured into ice-water, basified as above and steam-distilled. The solid was collected from the distillate and recrystallised from aqueous alcohol, m.p. 70-71°.

5-Chloro-8-aminoquinaldine.—5-Chloro-8-nitroquinaldine was similarly reduced as its 7-chloro isomer. When the reduction was completed, the mixture was cooled, made alkaline with sodium hydroxide and the aminoquinaldine was distilled with steam. The solid was collected and crystallised from aqueous alcohol, m.p. 92-93°. (Found: N, 14.12. $C_{10}H_9N_2Cl$ requires N, 14.54%).

BENGAL IMMUNITY RESEARCH INSTITUTE,
CALCUTTA.

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SYNTHESIS OF 8-AMINOQUINOLINES. PART VII*

BY ACHINTYA K. SEN AND U. P. BASU

Synthesis of 7-chloro-2-methyl-8-amino-4-(4′-hydroxy-3′-diethylaminomethyl)-anilinoquinaldine has been described.

During the course of a previous investigation on the synthesis of 8-aminoquinoline derivatives, simultaneously substituted at the 4-position by an aminocresol side chain, 7-chloro-8-amino-4-(4′-hydroxy-3′-diethylaminomethyl)-anilinoquinoline was synthesised (Chandran *et al.*, *J. Sci. Ind. Res.*, 1951, **10B**, 290). The compound showed signs of promise in the preliminary screening. From the metabolic study of quinine it is known that the drug undergoes oxidation in the system and forms a 2-hydroxy derivative (Mead and Koepfli, *J. Biol. Chem.*, 1944, **154**, 104). It was then considered to be of interest to substitute at the 2-position of the quinoline nucleus by a suitable grouping, and to see how the resulting quinoline would behave. Accordingly, a compound, analogous to the above compound but substituted at its 2-position by a methyl group, *i.e.* 7-chloro-2-methyl-8-amino-4-(4′-hydroxy-3′-diethylaminomethyl)-anilinoquinoline, has now been synthesised. The results of its preliminary screening tend to indicate high efficacy,.

7-Chloro-4-hydroxyquinaldine required in the present work was first prepared by Price *et al.* (*J. Amer. Chem. Soc.*, 1946, **68**, 1256) by the usual Conard-Limpach

* The present work was completed in 1953 on a project under the auspices of the Council of Scientific and Industrial Research. The publication was delayed due to one of the authors' (A. K. S.) mission to U.S.A.

method. The only isomer obtained in 72% yield was assigned the 7-chloro structure without establishing its constitution. Later work by Spivey and Curd (*J. Chem. Soc.*, 1949, 2656) records the yield of only 35-40% of the mixed 5- and 7-chloro isomeric compounds and they have separated the isomers through their corresponding picrates. It has now been found that the procedure followed by Price *et al.* furnishes a better yield, and contrary to their observation, it has been found that the 5-chloro isomer, which is invariably formed, remains in solution in the crystallisation liquor (aqueous alcohol) because of its relatively high solubility. The method described in the experimental part is found to be advantageous in our hands and it affords the desired 7-chloro isomer in a pure form in single crystallisation. A slight modification of the method of conversion of the hydroxy compound to the corresponding chloro compound has also been made in order to eliminate a violet-coloured dye which is also formed. 4:7-Dichloroquinaldine was nitrated in good yield to the corresponding 8-nitro derivative by potassium nitrate and 100% sulphuric acid. The nitro compound was reduced by stannous chloride in concentrated hydrochloric acid to the corresponding 8-amino derivative. In order to prove the position of the amino group, the amino compound was converted into 7-chloro-8-aminoquinaldine by catalytic hydrogenolysis. This was compared as picrate and as acetyl derivative with authentic samples of those derivatives from 7-chloro-8-aminoquinaldine (cf. this *issue*, p. 833). The melting points are identical and the mixed melting point determination of the sample shows no depression. The aminocresol side-chain was attached to the 4-position of the quinoline nucleus according to the method described by Burckhalter *et al.* (*J. Amer. Chem. Soc.*, 1948, **70**, 1363).

Experimental

7-Chloro-4-hydroxyquinaldine.—A mixture of *m*-chloroaniline (15 g.) and ethyl acetoacetate was mixed and kept under vacuum in a desiccator over calcium chloride until the theoretical amount of water was removed. The oily crotonate was added to boiling diphenyl oxide (260 c.c.). Heating was continued for 40 minutes more after the addition was over. The product separating from cooled diphenyl oxide was collected, washed thoroughly with acetone and dried; yield 13 g. The dried product was dissolved in rectified spirit (290 c.c.); after cooling 300 c.c. of water was added, heated to boiling and filtered hot. After keeping overnight the separated crystals were collected and dried, yield 8 g., m.p. 312-14° (Price *et al.* report m.p. 313-15°).

4:7-Dichloroquinaldine.—A mixture of 7-chloro-4-hydroxyquinaldine (20 g.) and $POCl_3$ (60 c.c.) was heated in an oil-bath under reflux for one hour. About half the quantity of excess of $POCl_3$ was distilled off under reduced pressure and the residual liquid was then poured into aqueous 50% NaOH solution (100 c.c.) to which enough ice was added to prevent the rise of temperature. The dichloro compound was collected, washed thoroughly with water and dried. After recrystallisation from aqueous alcohol, the compound melted at 103-104°; lit. m.p. 103°.

4:7-Dichloro-8-nitroquinaldine.—4:7-Dichloroquinaldine (10 g.) was dissolved in ice-cooled 100% H_2SO_4 (32 c.c.). Dried and powdered potassium nitrate (7.5 g.) was then added to the well-stirred acid mixture during one hour; the temperature was

not allowed to rise above 5° throughout the experiment. After the addition was over, the mixture was stirred at that temperature for 3 hours more and then kept in the refrigerator overnight. The mixture was then poured into ice-water (500 g.). The nitro compound separating was collected, washed thoroughly with water and twice crystallised from rectified spirit, yield 3.5 g., m. p. 120-21°. (Found: N, 10.54. $C_{10}H_6O_2N_2Cl_2$ requires N, 10.90%).

4 : 7-Dichloro-8-aminoquinaldine.—The preceding compound (5.28 g.) was slowly added to a stirred solution of stannous chloride dihydrate (19 g.), dissolved in HCl (75 c.c., conc.) during an hour, care being taken to keep the temperature below 30°. The mixture was stirred for 2 hours more and then poured into aqueous 50% NaOH (125 c.c.) to which enough ice was added to keep the temperature below 20°. The solid was collected, washed thoroughly with water and recrystallised from rectified spirit in a very light yellow crystalline solid, yield 3.5 g., m.p. 115°. (Found: N, 12.07. $C_{10}H_8N_2Cl_2$ requires N, 12.33%).

7-Chloro-8-aminoquinaldine.—To a solution of the above 8-aminoquinaldine (7.3 g.) in absolute alcohol (100 c.c.) fused sodium acetate (2.7 g.) and 5% palladium (0.5 g.) on carbon were added. The mixture was hydrogenated at normal pressure; the theoretical amount of hydrogen was taken up in 3 hours. The catalyst was filtered off and washed with two 25 c.c. portions of alcohol. After removal of the solvent the residue was treated with water, basified with a slight excess of aqueous caustic soda solution and extracted with ether. Ether solution was dried with KOH, ether removed and the residue was distilled under reduced preesure; b.p. 200-205°/10 mm. The melting point and mixed melting point determination of the acetyl derivative and of the picrate, prepared according to the method described in the preceding paper (this *issue*, p. 833), recorded no depression.

* *7-Chloro-2-methyl-8 amino-4-(4'-hydroxy-3'-diethylaminomethyl)-anilinoquinoline Dihydrochloride.*—A mixture of α-diethylamino-4-acetamido-*o*-cresol (5.5 g.) and HCl conc., 11 c.c.) was heated under reflux for 1 hour. After cooling and adjusting to p_H 4 with 50% caustic soda (aq.), 4 : 7-dichloro-8-aminoquinaldine (5 g.) was added and the mixture was heated under reflux for 5 hours on a water-bath. After keeping overnight, the mixture was triturated with a slight excess of ammonia (conc). The solid product was collected and washed thoroughly with water. The air-dried product was dissolved in 100 c.c. of rectified spirit and HCl (conc., 8 c.c.) was added to the solution; on stirring yellow crystalline hydrochloride of the base crystallised out. This was collected, washed with rectified spirit and finally crystallised from 70% ethyl alcohol, m.p. 258-60°. (Found: N, 11.68. $C_{21}H_{25}ON_4Cl,2HCl$ requires N, 12.21%).

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* This compound was investigated by the authors and the results communicated to the Council of Scientific and Industrial Research (India) on 28 Feb., 1953. The compound has also been independently investigated by Coatney and his co-workers (Surevey of Antimalarial Agents : U.S. Public Helth Service Monograph No. 9, Jan. 1953, p. 67).

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* SYNTHESIS OF CAMOQUIN ANALOGUES

By Achintya K. Sen and U. P. Basu

Synthesis of 2-methylcamoquin and the corresponding piperidinomethyl analogue has been described.

Metabolic studies on quinine (Mead and Koepfli, *J. Biol. Chem.*, 1944, **154**, 104) have demonstrated the formation of 2-hydroxyquinoline derivative in presence of liver. It was speculated that if the 2-position of the quinoline ring be blocked by a suitable grouping, there might be an enhancement of activity. This consideration was supported by the observation that α-(2-piperidyl)-2-phenyl-4-quinoline-methanol was much more effective against avian malaria than the corresponding compound without the 2-phenyl group (Raport *et al.*, *J. Amer. Chem. Soc.*, 1946, **68**, 2697). It was accordingly considered worthwhile to synthesise a 2-methyl analogue of 7-chloro-4-(4′-hydroxy-3′-diethylaminomethyl)-anilinoquinoline (Camoquin), in view of the pronounced antimalarial activity of the latter. The corresponding piperidinomethyl analogue was also synthesised. 7-Chloro 2-methyl-4-(4′-hydroxy-3′-diethylaminomethyl)-anilinoquinoline was synthesised by first condensing *p*-aminophenol with 4 : 7-dichloroquinaldine and the resulting condensate, 7-chloro-2-methyl-4-(4′-hydroxy)-anilinoquinoline was then subjected to the usual Mannich reaction with diethylamine and paraformaldehyde to furnish the desired compound. There are two vulnerable positions where the diethylaminomethyl group can enter, either at the position adjacent to the hydroxy group of the aniline or at the methyl group lying at the 2-positions of the quinoline nucleus. The identity of the resulting Mannich base has been established by its unambiguous synthesis from 4 : 7-dichloroquinaldine and 4-hydroxy-3-diethylaminomethylaniline, which indicates that the hydroxy group preferentially influences the reaction. The compounds were prepared according to the general method described by Burckhalter *et al.* (*J. Amer. Chem. Soc.*, 1948, **70**, 1363 ; 1950 **72**, 1024).

Experimental

7-Chloro-4-(4′hydroxy)-anilino-2-methylquinoline.—To a solution of *p*-aminophenol hydrochloride (4.85 g.) in water (50 c.c.) 4 : 7-dichloro-2-methylquinoline (7 g.) was added. The mixture was heated on a steam-bath for 4 hours and then allowed to stand for two days. The crystalline material was collected and stirred with excess of ammonia. The solid product was filtered off, washed thoroughly with water, dried in air and was then recrystallised from rectified spirit, m.p. 274-75°. (Found : N, 9.56. $C_{16}H_{13}ON_2Cl$ requires N, 9.81%).

* Covered by Indian Patent No. 52,003, April 7, 1956 (Council of Scientific and Industrial Research).

The present work was completed in 1953 on a project under the auspices of the Council of Scientific and Industrial Research. The publication was delayed due to one of the authors' (A.K.S.) mission to U.S.A.

7-Chloro - 4-(4' - hydroxy - 3'-diethylaminomethyl)-anilino-2-methylquinoline.—(*a*). 2-Diethylaminomethyl-4-acetamidophenol (6.4 g.) was heated under reflux with HCl (conc., 12.8 c.c.) for 1 hour. To the cooled solution, adjusted to p_H 4 by addition of 50% NaOH solution (aq.), 4 : 7-dichloroquinaldine (5.3 g.) was then added and the mixture heated on a water-bath for 3 hours. The oily liquid separating at the bottom solidified *en masse* in course of heating. The reaction mixture was then dissolved in 150 c.c. of hot water (charcoal), filtered, cooled and basified with a slight excess of ammonia. This was collected, washed thoroughly and was twice recrystallised from aqueous ethyl alcohol to afford a colorless crystalline solid, m.p. 183-84°. (Found: N, 11.06. $C_{21}H_{21}ON_3Cl$ requires N, 11 36%).

(*b*). A mixture of 7-chloro-2-methyl-4-(4'-hydroxy)-anilinoquinoline (8.7 g.), paraformaldehyde (1.0 g.), diethylamine (15 c.c.) and rectified spirit (30 c.c.) was heated under reflux for 8 hours on a water-bath. After the period the exeess of diethylamine and alcohol were evaporated off. The residue was dissolved in 3% HCl (200 c.c.), charcoaled and filtered. After cooling, the solution was basified with a slight excess of ammonia, filtered, washed thoroughly and sucked as dry as possible. The wet cake was dissolved in a minimum amount of rectified spirit (charcoal) and filtered. On cooling a crystalline solid separated. This was dried and twice recrystallised from aqueous ethyl alcohol, m.p. 183-84°. Mixed m.p. with the sample prepared by the method described above recorded no depression.

7-Chloro-4-(4'-hydroxy-3'-N-piperidylmethyl) - anilino - 2 - methylquinoline.—2-N-Piperidylmethyl-*p*-acetamidophenol (6.2 g.) was heated under reflux with 20% aqueous HCl (14 c.c.) for 1 hour. To the cold mixture, adjusted to p_H 4 with 20% aqueous NaOH solution (aq.), 4.7-dichloroquinaldine (5.3 g.) was added and heated on a steam bath for 4 hours. The solution was cooled, diluted with double its volume of water and basified with a slight excess of dilute ammonia. The solid was collected, washed thoroughly with water and recrystallised from rectified spirit, m.p. 120-21° (decomp.). (Found: N, 10.89. $C_{22}H_{24}ON_3Cl$ requires N, 11.00%).

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KINETICS OF THE REACTION BETWEEN HEXAVALENT CHROMIUM AND OXALATE, CATALYSED BY MANGANOUS SULPHATE

By Dhirendra Nath Chakravarty* and Satyeshwar Ghosh

The reaction between hexavalent chromium and oxalate has been specially studied in presence of manganous sulphate, which acts as a catalyst for the system. The temperature coefficient and the heat of activation for the catalysed reaction are calculated to be 2.932 and 19890 cals respectively against the values 1.915 and 11995 cals. for the uncatalysed system. The order of the reaction in presence of manganous sulphate tends to become unimolecular whilst without manganous sulphate it appears as trimolecular. These results suggest a change in the reaction mechanism in the presence of bivalent manganese.

The reaction between oxalate and hexavalent chromium is very slow. Dhar (*J. Chem. Soc.*, 1917, **111**, 707) showed the catalytic effect of hydrogen and bivalent manganese ions on this reaction velocity. According to him the order of this reaction in the presence of sulphuric acid is unusually high, being unimolecular with respect to chromic acid and trimolecular with respect to oxalate. Jablczusky (*Z. anorg. Chem.*, 1908, **68**, 38) postulated that the reduction of chromic acid by oxalic acid occurred in three stages, each one involving single electron change. Wagner (*ibid.*, 1928, **168**, 279) also suggested the existence of intermediate products in the interaction of chromic acid and oxalic acid solutions. The reaction between chromic acid and oxalic acid therefore appears to be complicated. Further, the part played by bivalent manganese in this reaction, according to the literature available, is strange in the sense that while it is a catalyst in the oxidation of oxalate, it has a retarding influence in the oxidation of alcohol, as it will be seen from our further communications.

In the present paper we have investigated the order of this chemical change, specially in the presence of bivalent manganese. It should be mentioned here that previous workers investigated this reaction in high acid medium which considerably masked the effect of bivalent manganese. Hence, our investigations are limited to low hydrogen-ion concentration. The hexavalent chromium used in these experiments is from potassium dichromate and where the reaction is carried out in the presence of bivalent manganese, mixtures of oxalate and oxalic acid have been used so that the hydrogen-ion concentration is not high. In some cases, however, acid concentrations have been increased by adding dilute sulphuric acid.

Experimental

Reagents of A. R. quality were used and the solutions prepared in the double-distilled conductivity water. Standardisation of the solutions was done by the usual volumetric and gravimetric methods. The reaction rate was followed by the iodometric estimation of the total oxidant left over at different time intervals. The reaction

* Present address: Dept. of Chemistry, University of Utah, Salt Lake City, U.S.A.

mixtures were kept in a precision thermostat (Townson and Mercer Ltd.) kept in a temperature-controlled room so that the variation of the temperature between the bath and the room was ± 0.5°. Two Jena bottles, one containing the oxalate and the other dichromate (and manganous sulphate where required) were first kept in the bath. On attainment of the desired temperature these were mixed together and the time was noted. At different intervals of time 5 c.c. of the reaction mixture was pipetted out and poured in the acidified potassium iodide solution to estimate quantitatively the amount of oxidant left over at that time against a standard sodium thiosulphate solution. Readings for the non-catalysed and catalysed reactions are recorded below.

Kinetics Data for the Reaction between Hexavalent Chromium and Oxalate in the absence of Bivalent Manganese

In the following table, the values of the temperature coefficient and the heat of activation are compiled for the reaction between hexavalent chromium and oxalate, when it occurs in the absence of the catalyst, manganous sulphate.

TABLE I

Initial overall conc. of oxalic acid = 0.05 *M*.

Initial overall conc. of potassium dichromate = 0.0033 *M*.

Temp.	Velocity constants. $k \times 10^3$.	Temp. coef. For 10° rise.	Mean.	Heat of activation. For 10° rise.	Mean.
25°	4.115	1.875		11480 cals.	
		(25°–35°)		(25°–35°)	
30°	5.466		1.915		11995 cals.
35°	7.720	1.955		12510	
		(30°–40°)		(30°–40°)	
40°	10.690				

The average value of the temperature coefficient between 25° and 40° isc alculated to be 1.915 for 10° rise and the average value of the heat of activation is approximately 12000 calories, a value which is sufficiently low. Experiments were also performed by regulating the concentrations of the reactants and for the above case when no manganous sulphate or sulphuric acid was used, the order was found to be 1 with respect to hexavalent chromium and 2 with respect to oxalate, and thus, the total order of the reaction was found to be 3.

Kinetics of the Reaction between Hexavalent Chromium and Oxalate in presence of Bivalent Manganese

The results of the catalytic effect of bivalent manganese on the reaction between hexavalent chromium and oxalate are presented below. Results parallel to those denoted in Table II are now put forward for the catalysed reaction.

TABLE II

Initial overall conc. of oxalic acid = 0.05 *M*.

Initial overall conc. of pot. dichromate = 0.0033 *M*.

Initial overall conc. of manganous sulphate = 0.00333 *M*.

Temp.	$k \times 10^3$.	Temp. coeff.		Heat of activation.	
		For 10° rise.	Mean.	For 10° rise.	Mean.
25°	11.71	3.077		20480 cals.	
30°	20.70	(25°–35°)	2.932	(25°–35°)	19890 cals.
35°	36.00	2.787		19300	
40°	57.70	(30°–40°)		(30°–40°)	

It is interesting to note here that the temperature coefficient of the catalysed reaction is higher than the temperature coefficient of the reaction when it is carried out in absence of bivalent manganese.

From the foregoing experiments, it is established that reaction between hexavalent chromium and oxalate is affected by the presence of manganous sulphate and acidity of the medium. In the following sections a thorough study was made on the order of reaction, calculated at various circumstances. The experimental procedure being similar, tables are only compiled for the different experiments performed.

Order of Reaction with Sulphuric Acid and without Manganous Sulphate

TABLE III

Overall conc. of $K_2Cr_2O_7$ = 0.0033 *M* and that of H_2SO_4 = 0.5 *N*. Temp. = 30°.

A. Potassium acid oxalate = 0.05 *M*.			B. Potassium acid oxalate = 0.1 *M*.		
Time.	0.1 *N*-$Na_2S_2O_3$.	$k \times 10^3$.	Time.	0.1 *N*-$Na_2S_2O_3$.	$k \times 10^3$.
2 mins.	3.70 c.c.	...	2 mins.	3.42 c.c.	...
10	3.26	15.83	5	2.80	66.63
20	2.72	17.09	9	2.00	71.03
25	2.54	16.36	12	1.72	68.74
30	2.32	16.67	15	1.40	61.02
35	2.14	16.60	20	1.02	67.22
40	1.98	16.45	23	0.82	69.19
		Mean 16.46			Mean 67.30

From the above table the order of the reaction is calculated to be 2.03, showing thereby again the bimolecular nature of the reaction with respect to oxalate. It is also shown from the velocity constants that the reaction becomes faster with the addition of sulphuric acid in the system.

Order of Reaction in presence of different amounts of Manganous Sulphate and without Sulphuric Acid

TABLE IV

Overall conc. of $K_2Cr_2O_7$ = 0.0033 *M* and that of $MnSO_4$ = 0.002*M*. Temp. = 30°.

A. Potassium acid oxalate. = 0.05 *M*.

Time.	0.1 *N*-$Na_2S_2O_3$.	$k \times 10^3$.
0 min.	8.73 c.c.	...
3	8.40	13.97
7	7.94	14.05
12	7.48	13.16
16	7.10	13.13
20	6.82	12.56
25	6.44	12.31
30	6.04	12.40
35	5.70	12.28
	Mean	12.98

B. Potassium acid oxalate. = 0.1 *M*.

Time.	0.1 *N*-$Na_2S_2O_3$.	$k \times 10^3$.
0 min.	8.76 c.c.	...
3	8 20	22.03
6	7.84	18.50
10	7.36	17.41
15	6.80	16.35
20	6.30	16.48
25	5.86	16.08
30	5.38	16.25
35	4.92	16.48
	Mean	17 45

TABLE V

Overall conc. of $K_2Cr_2O_7$ = 0.0033 *M* and that of $MnSO_4$ = 0.006 *M*. Temp. = 30°.

A. Potassium acid oxalate = 0.05 *M*.

Time.	0.1-*N*-$Na_2S_2O_3$.	$k \times 10^3$.
0 min.	8.76 c.c.	...
3	7.80	38.68
7	6.74	37.30
11	5.84	36.87
15	5.00	37.38
20	4.20	36.72
25	3.46	37.16
30	2.80	38.02
35	2.30	38.21
	Mean	37.54

B. Potassium acid oxalate = 0.1 *M*.

Time.	0.1-*N*-$Na_2S_2O_3$.	$k \times 10^3$.
0 min.	8.76 c.c.	...
3	7.52	50.89
7	6.54	43.95
11	5.48	42 47
15	4.54	43.72
20	3.60	44.47
25	2.80	45.63
30	2.24	45.50
35	1.70	46.85
	Mean	45.43

In presence of manganous sulphate of final concentration 0.002 *M*, the order of the reaction is found out to be equal to 0.43 with respect to oxalate. When more of manganous sulphate is added, e.g. of final strength 0.006 *M*, the order with respect to oxalate goes down to 0.27, and thus, the total order tends to unity.

Order of Reaction in presence of both Manganous Sulphate and Sulphuric Acid

TABLE VI

Overall conc. of $K_2Cr_2O_7$ = 0.0033 *M* and that of $MnSO_4$ = 0.002 *M* and of H_2SO_4 = 0.5 *N*. Temp. = 30°.

A. Potassium acid oxalate = 0.05 *M*.

Time.	0.1 *N*-$Na_2S_2O_3$.	$k \times 10^3$.
2 mins.	3.60 c.c.	...
7	2,60	65.56
10	2.08	68.56
13	1.70	68.23
15	1.48	68.37
18	1.20	68.78
	Mean	67.78

B. Potassium acid oxalate = 0.1 *M*.

Time.	0.1 *N*-$Na_2S_2O_3$.	$k \times 10^3$.
2 mins.	3.26 c.c.	...
4	2.50	132.76
6	1.84	143.01
8	1.30	136 60
11	0.88	145.52
13	0.60	153.90
15	0.34	150.67
	Mean	143.74

The order for the above set is calculated to be 1.07 with respect to oxalate. Thus, the total order becomes equal to 2. This value for the order of reaction in presence of sulphuric acid shows that the catalytic effect of manganous sulphate is minimised in presence of sulphuric acid in the system, which is obvious because of the fact that sulphuric acid itself enhances the reaction.

Generally a reaction with lower value of activation energy for a chemical reaction leads to its greater velocity at ordinary temperatures. But it is noted from Tables I and II that though the rate of oxidation of oxalate by hexavalent chromium is considerably increased in presence of manganous sulphate, yet there is a considerable increase in the reaction velocity. The velocity constant of a reaction can be represented by (cf. Theory of Absolute Reaction Rate):

$$k_r = (kT/h).\ e^{\Delta S/R}\ .\ e^{-E_a/RT}$$

where ΔS is the entropy of activation, E_a is the heat of activation, and k_r, the velocity constant.

From the above expression we find that the value of k_r is dependent on the value of ΔS and E_a. It appears therefore that the value ΔS is highly increased in the presence of manganous sulphate, so much so that the velocity of the reaction becomes large, though the heat of activation is also increased. This indicates that the reaction mechanism of the oxidation of oxalate by hexavalent chromium involves different species of ions than those reacting in the absence of bivalent manganese (cf. Frost and Pearson, "Kinetics and Mechanisms", John Wiley and Sons, Inc., 1952).

Conclusion

From the experimental observations presented in this paper on the reaction between hexavalent chromium and oxalate, the following salient features may be noted:

1. The oxidation of oxalate by hexavalent chromium is unimolecular with respect to the latter, but the order with respect to the former considerably changes as the reaction is catalysed by the acid or by bivalent manganese.

2. In presence of sulphuric acid the order with respect to oxalate is 2 or even 3, but it has a tendency to fall down to zero with increasing concentration of bivalent manganese. Thus, a changed mechanism of the reaction, when occurring in presence of manganous sulphate, is expected.

3. The temperature coefficient and the heat of activation also lead to the similar conclusion. The rule of Dhar (*Z. anorg. Chem.*, 1923, **128**, 218) that greater the order of chemical reaction, smaller the temperature coefficient, has been found to be true.

Thanks are due to the Ministry of Education, Government of India for the award of a senior research scholarship to one of the authors (D.N.C.) which enabled him to undertake this work.

Chemical Laboratories,
University of Allahabad,
Allahabad-2.

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REVIEWS

Fundamentals of Chromatography.—By Harold G. Cassidy. Vol. X of the Weissberger Series: Technique of Organic Chemistry. Published by Interscience Publishers Inc., New York, 957. Pp. 447 + xvii. Price $ 9.75.

The volume under review, as explained in the preface by the Editor, is the outcome of an attempt to revise the Chapters on Chromatography which appeared in Vol. V of the Weissberger Series under the caption "Adsorption and Chromatography". The author explains in his preface the reasons for a new book on chromatography alone written from a new point of view.

Chromatography with its varied offshoots has become a formidable tool in the hands of chemists. As it often happens, the practice and technique become much more familiar than the principles involved. This remark is especially pertinent to the technique of chromatography. A critical appreciation of the theories and principles formulated by different workers has not been forthcoming. Chapter IV on General Theory fills up this inadequacy by providing a connected account of the broad principles in a simple manner, leaving out the intricacies. For those who are interested in a general outline of the principles of chromatography, this account is excellent. It also brings out clearly how a general principle runs through the apparently different procedures.

The plan of dividing each chapter dealing with a particular technique into principles, classification, apparatus, procedures and modifications together with copious examples of applications shows the cautious effort of the author to make the book highly useful to its readers. There are numerous practical hints, meant primarily for actual workers, about the different techniques discussed in the separate chapters, but chapters XII-XV dealing with recognising and evaluating zones, relation of Rand R_f to molecular structure, choice of mobile and stationary phases and a systematic scheme of chromatographic separation show the meticulous care with which the book has been prepared. In fact, one hardly misses the author's careful planning of the book and the desire to make it sufficiently helpful. Chapter XIII on the relation of Rand R_f to molecular structure is likely to evince further interest along this line.

The sources of chromatographic equipment, addresses of industrial firms dealing with chromatography in one form or the other, listed in the appendix, and the list of up-to-date references numbering more than one thousand, carefully compiled by the author, are some of the other attractive features of the book.

S.K.M.

Vitamins and Hormones.—Edited by Robert S. Marris, G. F. Marian and Kenneth V. Thimann. Vol. XIV. Pp. 486 + xi. Published by Academic Press Inc. Publishers, New York, 1956.

The present volume is in series of annual publications on the recent advances in vitamin and hormone researches. It has maintained the high standard and tradition of

its predecessors. Its contributors are all eminent workers in their respective fields. The first two chapters deal with vitamins—one relates to the intestinal synthesis of vitamins in nonruminants and its importance in the nutrition of the host, and the other article discusses some aspects of vitamin-A metabolism. Large amounts of many vitamins are synthesised by the bacteria inhabiting the intestinal tract of animals. In the case of nonruminants, only a few vitamins are utilised by direct absorption unlike in the case of ruminants where the requirement for water-soluble vitamins is almost fully satisfied from the intestinal synthesis. Not much work has been done so far to determine which of the specific requirments for vitamins are satisfied by intestinal synthesis in human being. There is a suggestive evidence that many adults secure a part of their pyridoxine and vitamin B_{12} from this source. The author has also reviewed the work of the effect of antimicrobial compounds, including antibiotics on the intestinal microflora and its influence on the nutrition of the animal. It seems that though some growth promoting effects are observed in certain cases on administration of antimicrobial compounds, the exact mechanism of the change that is brought about is not known.

In the vitamin-A metabolism, the author points out that although much progress has been made in describing the deficiency syndrome and the effect of vitamin A on visual process, its mode of action in promoting the growth and maintaining the usual status in the body is considered obscure. The site and mechanism of synthesis are described in details, particularly the latest work of Glove and Redfearn who suggest that the initial attack on β-carotene occurs at the end of the molecule and proceeds by β-oxidation until retinene is formed, reduced to vitamin A and finally absorbed. Then the mode of action of vitamin A on protein and amino-acid metabolism, hormonal action, particularly pituitary adrenal function, oxidative mechanism, hyperkeratosis, as far as they are known up to the present, are described. The authors feel that the vitamin has its own peculiar mode of action which must not be studied in isolation.

In the two chapters on the hormonal control of carbohydrate metabolism, the first deals with the effect of hormones at different sites of carbohydrate metabolism - muscle, liver, kidney, brain, retina etc. It helps one to get in a single article all the available information on the behaviour of different tissues during carbohydrate metabolism and how it is regulated under normal and abnormal conditions. The next article describes the syndrome of diabetes mellitus, occurring clinically and produced experimentally not primarily due to lack of insulin. Thus pituitary hyperglycemias, adrenal hyperglycemias, pancreatic hyperglycemias, renal, thyroid and estrogenic hyperglycemias are all described giving their particular features and the over-all relation to each other. It is quite interesting to observe that although secretions from every endocrine gland are associated with hyperglycemia, only insulin is always hypoglycemic.

Biochemical studies on insect hormones is probably the first of a detailed review on the subject and biochemists and zoologists alike would find it highly stimulating. As in the case of vertebrates, the insects also have a highly developed system of endocrine glands. The principle of a dominant hormone, as we know from the hypophyses of vertebrates, has its counterpart in neurosecretory cells of insects. The morphogenesis of insects can also be followed with the hormonal regulation of development. The biological basis of the hormones is, however, incompletely understood.

The other articles deal successively with glucoronide metabolism, bioassay of gonadotropins and microbiological transformation of steroids. Whereas the enzyme β-glucoronidase is present widely in the animal body and participates in the hydrolysis of naturally occurring glucoronides of steroid, and nonsteroid alcohols and phenols, the enzyme-synthesising conjugated glucoronides from glycogen and aglycones are present only in liver and kidney. It is still not known whether the same synthetic system is involved in the production of chondriotin and hyaluronic acid.

The increasing importance of steroids in clinical use has heightened interest in their synthesis and interconversion by different means, the most interesting being those brought about by micro-organisms. The article provides a list of the number of steroidal transformations brought about by a large number of micro-organisms, some of which have been commercially exploited as in the case of antibiotics manufacture. The technique of paper chromatography has once again come to be particularly useful in the detection and studies of the microbial changes of steroids. General description is given of the fermentation processes and the isolation methods, and the reader is referred to other articles of interest dealing with the subject.

All the chapters have at their ends quite a comprehensive list of references. At the end of the book there are also author and subject indexes. The book as a whole will be widely appreciated by all workers in the field of vitamin and hormone research and is an extremely useful addition to the recent publications on this particular field of Biochemistry.

S. G. & S. C. R.

Synthetic Polypeptides.—By C. H. Bamford, A. Elliot and W. E. Hanby. Published by Academic Press Inc. Publishers, New York, 1956. Pp. 445 + xiii.

In this period of rapid scientific progress, there are two opposing demands for scientific literature. On the one hand, there is always the demand for a comprehensive treatise on a given subject for specialists working in it. On the other, there is also a demand for a concise summary of the subject for those who wish to keep pace with progress outside their particular field. Then again, there are certain border-line subjects which are of interest to chemists and physicists as well. Books on those subjects are written for one class of workers or other and special emphasis is laid either on the physical or on the chemical aspect of the problem.

Synthetic polypeptides form one such border-line subject, but Bamford, Elliot and Hanby's book is one written for those interested in the subject of proteins in general and polypeptides in particular, irrespective of their faith and belief. Thus organic chemists will find in this book a thorough and up-to-date review of the various methods of preparation of synthetic polypeptides and the probable mechanism involved in their formation ; the physical chemists will find what is probably the best account of the physico-chemical methods used in the detection of the presence of hydrogen bonds and the role of such bonding in determining the characteristic properties of these compounds, and the physicists will find their X-ray diffraction echniquesi n actioni n a complex field.

To some it may appear that rather too much stress has been laid on the role of hydrogen bonding, but the reviewer feels that the importance of hydrogen bonding in these systems cannot be overestimated and the authors have done proper justice to the whole subject, although what exactly is the nature of these bonds and what type of interactions are involved in these bond formation have not been clearly explained. The book contains one chapter on Silk protein which according to reviewer is the best account of the physico-chemical aspects of silk fibroin existing in chemical literature.

The book is unquestionably a remarkable achievement, presenting a wealth of information in an eminently readable form. As a general review it is certainly unsurpassed, but its standard will greatly limit the number of general readers, who will wish to read it through. The experts, on the other hand, will find it sufficiently detailed to be helpful in his own subject, be it organic chemistry, physical chemistry or physics. Workers in one particular field can benefit by dipping into other sections to see what their fellow workers are doing and in so doing may well find fresh ideas.

There is one great defect in this book which the reviewer considers his duty to point out. The book contains no authors index. Let us hope that this will be included in the next printing. S. B.

Dictionary of Organic Compounds: 4 Volumes.—By Prof. Sir Ian Heilbron, D. Sc., LL. D., F.R.I.C., F.R.S. and H. M. Bunbury, M. Sc., F.R.I.C. Published by Eyre & Spottiswoode, 15 Bedford Street, London W C. 2, 1953. Price £ 7/-each.

Heilbron's "Dictionary of Organic Compounds" was first published during the period 1934 and 1937, in three volumes and it gained enormous popularity among the research workers interested in organic compounds. The second edition of the book appeared in November 1953 in four volumes.

In this new edition not only over 2500 new entries are included but also some thousands of additions or amendments have been made to the previous entries. Important recent references have been incorporated in many cases and in some cases references of research work of 1953 have also been included. The mode of presentation in the new edition remains the same as in the previous edition. Due to the inclusion of a large number of compounds the Dictionary has become a standard reference book.

In each short monograph molecular and structural formulae, physico-chemical properties, functional derivatives and important references covering various informations regarding the compounds are given. The authors deserve thanks for their effort in revising the Dictionary. B.P.

Advances in Carbohydrate Chemistry: Vol. XI.—Edited by Melville L. Wolfram. Published by the Academic Press Inc. Publishers, New York, 1956, 465 + vii pages. Price $ 11.00.

The present volume is uniform in standard with its preceeding ten volumes. Its contributors have been selected from several countries—England, Scotland, Canada, Spain and the United States to bring close together contemporary research workers in different fields of carbohydrates. The specialised articles on Pericdate oxidation of carbohydrates by J. M. Bobbitt, the Osazones by S. Bayne and J. A. Fewster, Reactions of monosaccharides with β-ketonic esters and related substances by F. Garcia Gonzalez, Kojic acid by A. Beelik, Biosynthesis of monosaccharides by L. Hough, Branched-

chain sugars of natural occurrence by F. Shafizadeh, Nucleic acids by Barker, and Aspects of the physical chemistry of starch by C. T. Greenwood are indispensable to serious students of carbohydrate chemistry. The chapters on periodate oxidation of carbohydrates and kojic acid are the most interesting reading for students and teachers of organic and bio-chemistry whose special study is not exactly carbohydrates.

R. C.

Introduction to Physical Chemistry : Vol. I.—By S. N. Mukherjee, D. Sc., Professor of Physical Chemistry, Jadavpur University. Published by Art Union, Calcutta, 427 pages.

This is a well-written book for the students who want a clear introduction to principles of Physical Chemistry. It will certainly be a useful book for the Honours and Post Graduate students of our University and the teachers also will be gratified to see this introductory text.

In the first volume the author has included seventeen chapters covering the kinetic theory of matter, the two laws of thermodynamics, liquid and solid states of aggregation and the properties of solutions. The treatment is quite lucid and yet every topic has been developed from mathematical stand-point. The work reflects the experience of a seasoned teacher. Many cases, where the beginners are likely to be confused, have been specially explained and developed. The treatment of the Van der Waal's equation or coefficient of viscosity will bear this out.

One special and a very good feature of the book is that the author has throughout been very careful to impress upon the readers the necessity of use of proper units. The well-chosen problems at the end of the chapter will be appreciated by students. The chapters II and III could, however, be condensed considerably. The treatment of the 'solid state of aggregation' should have been a little more elaborate. In comparison to other chapters this has been very much compressed. The simple applications of the laws of thermodynamics have been nicely illustrated but the discussion on some more statements of the second law other than those of Clausius and Kelvin would be appreciated. The author mentions only, "Many special statements of this law can be made .....". There are, however, quite a number of printing mistakes, which it is hoped, will disappear in its next publication.

Altogether the book is a nice presentation of the fundamental principles of Chemistry that will stimulate the knowledge-hungry students. Even a moderately bright student with some knowledge of calculus will find this book an excellent diet indeed.

P. C. R.

Commercial Waxes.—Edited by H. Bannett. Published by the Chemical Publishing Co. Inc., N.Y., U.S.A., pp. 688. Price $ 15.00.

The book under review is the enlarged and revised edition of the original one. It deals with both natural and synthetic commercial waxes. The physical and chemical properties of these waxes and their mixtures and solutions have been recorded in tabulated forms. These are generally not available in detail. The chapter on analysis, identification, detection of adulteration provides an additional interest. The chapters on uses and formulary respectively will be of interest to the expert as well as to a beginner.

There are some printing lapses which are expected to be removed, e.g. page 277 figure 53, instead of % paraffin it should be specific gravity.

A. N. S.

Physical Methods in Chemical Analysis: Vol. III.—Edited by Dr. Walter G. Berl. Published by Academic Press Inc. Publishers. New York, 1956. Pp. 652+xii. Price $ 13.50.

Review articles such as those that are presented in the present series serve several useful purposes. One of these is the information they convey particularly to the chemist of physical tools which he can use with great advantage for his research and routine work. The adaptation of physical techniques to analytical purposes is taking place so rapidly that the chemist cannot remain satisfied without equipping himself with the latest improvements and new innovations. The development of the techniques is the outcome of a constant need for more and more accurate, rapid and sensitive methods which would unravel the details not only on a macro level but also on a molecular level. The techniques are often quite complicated and their principles, more so. Thanks to the manufacturing firms, most of the physical tools are now available in almost fool-proof condition. But even then for the interpretation of results or for adaptation to a different set of experiments, a sound knowledge of the theoretical principles as well as the constructional intricacies is essential. The object of the book is to render a useful service to the chemists, and hence, the articles although written by specialists are not meant for the specialists alone. The treatment of each is according to a more or less general plan: introduction; theory; apparatus & techniques; modifications, if any. Applications and a full reference to earlier and recent work up to 1956, appropriate illustrations, practical hints, reference to and description of available equipments and particularly the scope and limitation concerning each apparatus and method are important features of the book.

Some of the articles, as one can see, supplement and extend very effectively the scope of those published in Volumes. I and II and thereby the desirable link between the three volumes has been maintained. Some of the techniques, viz., field ion microscopy and neutron activation, although not yet within the compass of every-day use, are destined, as the Editor puts it, to open up "regions of versatility and sensitivity of detection unmatched by any other techniques." By bringing out this and the previous two volumes of this series, Dr. Berl has rendered a very useful service to the practising chemists and students of advanced instrumentation. The established reputation of the Publishers has been maintained throughout the book.

S. K. M.

OBITUARY

Sir John Lionel Simonsen

Born : 1884. Died : Feb. 20, 1957.

Dr. R. C. Cahn (*Nature*, 1957, **179**, 697) has mentioned that in the death of Sir John Lionel Simonsen on 20th February, 1957, England has lost one of the last of the chemists trained in the Edwardian experimental tradition.

Born in 1884 of Danish parentage, Sir John had his early education at Manchester Grammar School. Studying contemporaneously with Sir Robert Robinson, Sir Norman Haworth and Professor C. S. Gibson at the Victoria University, Manchester, he obtained first-class honours in chemistry under Professor W. H. Perkin Jr.

During the six years (1904-1910) of his post-graduate career in Manchester, he worked first as a research fellow and later as a lecturer. Sir John spent the next seventeen years (1910-1927) in India where he held different assignments. From 1910 to 1919 he was Professor of Chemistry, Presidency College, Madras ; from 1919 to 1925 he was the Chief Chemist, Forest Research Institute and College, Dehra Dun ; from 1925 to 1927 he was Professor of Organic Chemistry, Indian Institute of Science, Bangalore. After returning to England, he was appointed as the Professor of Chemistry at the University College of North Wales, Bangor, for twelve yeras (1930-1942). From 1942 to 1952 Sir John was the Director of Colonial Products Research Institute, South Kensington, London.

Sir John's major contribution to organic chemical research was in the field of essential oils and terpenes. He and his collaborators, among whom figured a number of Indians, have published about 175 research papers in different journals and bulletins. He was an authority in this field of investigation. This fact is borne out by the recognition of his book entitled "The Terpenes" as a standard work on the subject. The first edition (1930-32), published in two volumes, comprised work on mono- and bi-cyclic terpenes. The second edition, covering higher terpenes as well, and running into five volumes, is written in collaboration with Professors L. N. Owen, D.H.R. Barton and C.W.J. Ross.

Sir John took keen interest in scientific organizations and was actively connected with many. He was one of the prime-movers and founder members of the Indian Science Congress Association, started in 1914. He was its General Secretary from 1914 to 1926. He presided over the session of the Indian Science Congress held in 1928. He was also actively associated with the Indian Chemical Society and served the Society for several years as Vice-President and a Member of the Council. During World War I, Sir John served as Controller of Oils and Chemical Adviser to the Indian Munitions Board. He and Sir Robert Robinson were primarily responsible for the establishment of a Microbiological Research Institute at Trinidad. He was Hony. Secretary of the Chemical Society, London, during 1945-49 and later, a Vice-President. He served

as a member of the Council of the Royal Society of Arts, London, and as Hony. Treasurer of the Laws Agricultural Trust, Rothamstead. He presided over the Section of Chemistry at the British Association meeting in 1947.

Sir John was the recipient of many academic and public honours. He was elected a Fellow of the Royal Society in 1932. Some of the awards were :—Honorary D.Sc. degree by the Birmingham and Malaya Universities and LL. D. degree by St. Andrews ; Kaiser-i-Hind Silver Medal (1921) ; Kinghthood (1949) ; Davy Medal (1950) ; and Fritzsche Award of the American Chemical Society (1949) [vide *J. Royal Inst. Chem.*, 1957, **81**, 658 ; *J. Royal Soc. Arts*, 1957, **CV**, 265].

Paying a warm tribute, Sir Robert Robinson (*Nature*, 1957, **179**, 698) has said that Sir John "was a most elegant experimentalist" whose "unusual talent for handling alicyclic substances led him into his brilliant excursions in the field of higher terpene chemistry. He (Sir John) was a most lovable person, incapable of any mean action, transparently sincere in all his relations, personal and scientific".

Sir John married in 1913 Dr. Jennet Dick Hendrie who was then in charge of the Lady Dufferin Hospital, Madras.

The writer of this note recalls with pleasant memories the cordial welcome extended to him when he called on Sir John at the Colonial Products Research Institute in October, 1950. Sir John loved India and the Indian workers. He played a notable part in the development of scientific research in this country. May his soul rest in peace!

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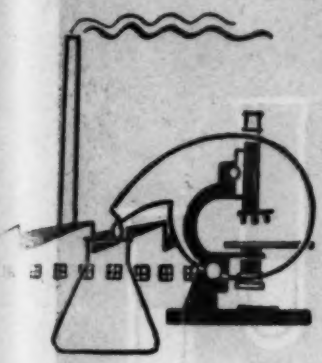

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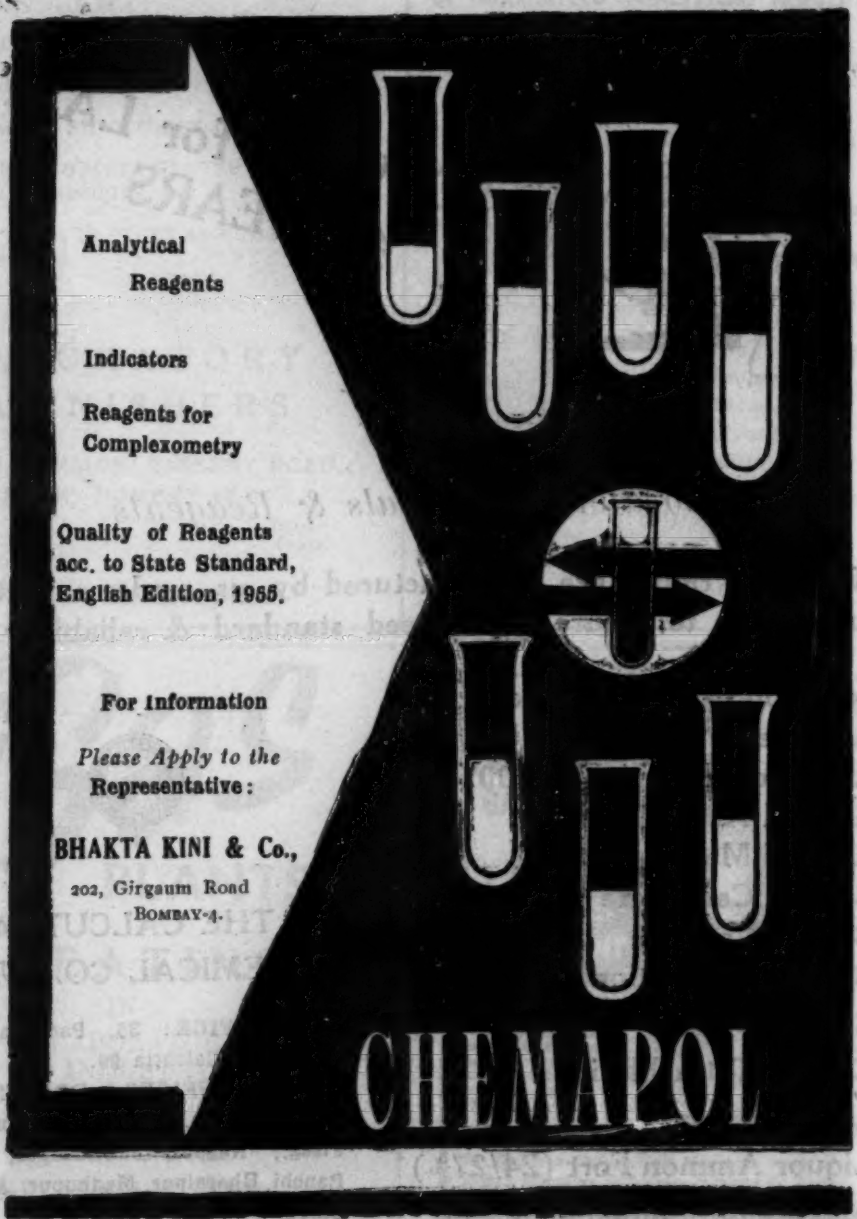

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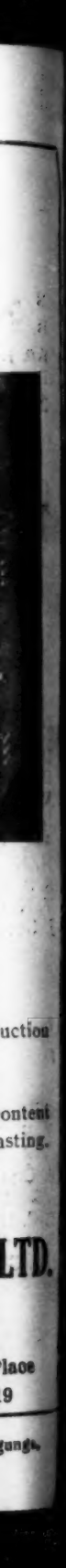
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